SCATTERING OF LIGHT
AND
THE RAMAN EFFECT

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PREFACE

This volume is an outcome of a course of lectures which the author has been giving to some of the post-graduate students at the Andhra University during the past five years. It is a connected account of the subjects of scattering of light and the Raman effect. The outlook of the book is mainly experimental, although a fair amount of mathematical detail, which is considered necessary for a proper understanding of the subject, is included in the appropriate places. Most of the chapters form an easy reading. Chapters XI and XII, where a working knowledge of the principles of wave-mechanics and certain standard theorems of tensor algebra and group theory have been assumed, may be omitted in the first reading, if found necessary.

It is now well known that, although the subject is of comparatively recent origin, a vast amount of literature has grown around it. In a single volume like this, it would be impossible to do justice to all the different branches of science in which it has found application. The treatment is accordingly confined, in the main, to the physical aspects. No attempt is made to give comprehensive references to literature, because several useful bibliographies have already been published. The early work relating to Rayleigh scattering and the more recent developments connected with the discovery and applications of the Raman effect have been brought together in this book with a view to emphasize the close relationship between them. This appears entirely appropriate in view of the fact that the discovery of the Raman effect was the result of the intensive experimental investigations that were carried on by Professor Raman and his collaborators in the field of Rayleigh scattering.

Several Universities are beginning to include this subject as part of their curricula in advanced physics. A student, who desires to undergo such a course, now finds that much of the information he needs is scattered in various scientific journals. It is hoped that this book, which is an attempt in the direction of bringing it all together and presenting a connected account

of the underlying theories and experimental facts, will serve a real need.

The author desires to take this opportunity for expressing his grateful thanks to Professor Sir C. V. Raman. Without his constant advice and kind encouragement, it would not have been possible to prepare this volume.

Figs. 6, 11, 14 and 16 are taken from *La Diffusion Moleculaire de La Lumiere* by Prof. J. Cabannes. Figs. 7, 8, 17, 35 and 36 are taken from the *Proceedings of the Royal Society* of London. Figs. 9, 12 and 31 are taken from the *Indian Journal of Physics.* Figs. 13, 25, 26 and 32 are taken from the *Proceedings of the Indian Academy of Sciences.* Figs. 30 and 38 are taken respectively from the *Physical Review* and the *Journal of Chemical Physics.* Figs. 37 and 39 are taken from *The Raman Effect and its Chemical Applications* by Dr. J. H. Hibben. Fig. 28 is taken from *Der Smekal Raman Effect* by Prof. K. W. F. Kohlrausch. Fig. 10 is due to Dr. J. Weiler. The Raman spectra of O_2 and N_2, reproduced in Plate II, are those originally obtained by Dr. Rasetti. The Raman spectrum of diamond, reproduced in Plate I, has been kindly supplied by Mr. P. G. N. Nayar. The author, while acknowledging the sources from which all the above figures have been obtained, desires to express his grateful thanks to all the concerned authorities of the various journals who have given him permission to reproduce the figures.

S. BHAGAVANTAM.

FOREWORD

The author of this book has been the most assiduous investigator in India in the field of Physics with which it deals during the past ten years. He has made many significant contributions to the subject, the value of which has been widely recognized. Professor Bhagavantam has also successfully introduced the subject to numerous aspirants for a scientific career. Indeed, Professor Bhagavantam's enthusiasm and capacity as a teacher and leader of research at the Andhra University are well known. It is very appropriate, therefore, that he has undertaken the task of giving a systematic exposition of the subject. I feel sure that the treatise he has written will be found most useful and will win appreciation, both in and outside India.

The field of research covered by the book, though extensively cultivated, has not yet yielded all the results that it is capable of. Especially in the study of the solid state is there much valuable work waiting to be done. Professor Bhagavantam's treatise will, I greatly hope, encourage further research by making the results already reached more widely known and more readily accessible to the investigator.

C. V. RAMAN.

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Chapter I

SOME NATURAL OPTICAL PHENOMENA

Reflection and Refraction of Light.—It has been known for quite a long time now that the phenomena of reflection and refraction occur only when light falls on a boundary separating two media of different refractive indices. No such thing happens to a beam of light when it traverses a medium which is continuous and uniform. Visibility of matter, which is not self-luminous, was accordingly attributed until very recently to irregular reflection taking place at the surface. It was tacitly assumed that there is no lateral radiation emitted from within a transparent body when it is traversed by a beam of light. This common belief could easily be supported and proved to be in accordance with theory in the case of a perfectly transparent, structureless and homogeneous medium as the result depended upon a complete destructive interference of all the secondary waves coming in a lateral direction. It is, however, obvious that on account of thermal agitation, no medium may be regarded as perfectly homogeneous. Consequently, there is bound to be a residual effect although small. That such an effect, which may be called lateral diffusion, actually exists and is as much a common property of all transparent matter as any other optical property such as refraction, has been realized only very recently. This realization has been the starting point of the subject of light scattering which is to-day an important branch of physics.

Diffusion of Light.—We now know that light is diffused laterally with varying degrees of intensity by matter in all states of aggregation. No special arrangements are needed and it is quite easy to demonstrate the effect in liquids. When a beam of white light is condensed by means of a lens into the centre of a large glass bulb containing a dust-free liquid such as benzene, an observer who shields himself from the light coming directly from the source and views the track in the liquid in an oblique direction will at once see a magnificent blue scattering. The

experiment is easily performed by allowing sun-light to enter a darkened chamber through a suitable aperture. The colour of the scattered light strongly resembles the deep blue colour exhibited by the sky on a clear and cloudless day. Any other liquid may be substituted for benzene and the effect persists but with a different intensity in each case. Matter in the form of clear and transparent solids, either crystalline or amorphous, and gases free from dust as well may be shown to behave in an exactly similar manner by adopting somewhat similar but improved arrangements which are necessitated by the fact that the intensity of the scattered light is rather low in these cases. These experiments clearly show that the diffusion of light is a universal property of matter and is subject to definite laws which are intimately connected with its state of aggregation. This important conclusion, which may be to-day regarded as an established fact, has its beginnings in the attempts by the early scientific men to find a satisfactory explanation of a number of natural optical phenomena. We shall now describe the main features of three such cases, the blue colour of the sky, the blue colour of the oceanic waters, and the blue colour exhibited by thick layers of transparent ice blocks such as those occurring in glaciers, as illustrations respectively of matter in the gaseous, liquid and solid states diffusing light.

Blue of the Sky.—The blue colour of the sky is a most familiar and conspicuous example of a natural optical phenomenon that has arrested the attention of the early philosophers. Of the many explanations that were repeatedly offered, the one that was put forward by Leonardo da Vinci is of special interest as he was the first to attribute the colour to the suspended particles in air. Tyndall,[1] amongst other observers, prepared a large number of clouds or *artificial atmospheres*[2] and

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[1] Phil. Mag., *37*, 384 (1869).

[2] Examples of such clouds prepared by Tyndall are quite numerous and they usually consisted of fine solid particles obtained by the decomposing action of light on some organic substance such as, for instance, vapour of allyl iodide. Amongst other substances suitable for producing the Tyndall phenomenon, mention may be made of a mixture of air bubbled through butyl nitrate with air that is bubbled through hydrochloric acid. The total pressure

studied the diffusion of light by these clouds on a laboratory scale. This phenomenon of the scattering of light by colloidal solutions or turbid media has now come to be known as the Tyndall effect. Characteristics exhibited by the light scattered by such clouds or *artificial atmospheres* are quite numerous and complicated. Here it is not proposed to go into the details of these complicated phenomena as they properly come under the subject of colloid optics. The features exhibited by this type of scattering stand in marked contrast to those that are met with in molecular scattering as we shall see later.

Tyndall found an analogy between the blue of the sky and the blue of the light scattered by such *artificial clouds* in the intial stages and expressed the view that the atmosphere should be regarded as a turbid medium since numerous particles composed of dust, drops of water, minute crystals of ice, etc., float in it. As such, it may be expected to diffuse the incident sun-light in all directions in a manner closely analogous to an *artificial cloud* prepared in a laboratory. If this view is accepted, the blue of the sky stands at once explained. Tyndall's explanation for the blue of the sky was, however, generally and widely accepted only till about the end of the nineteenth century, when the fundamental question as to what is the precise nature of the small particles that float in the atmosphere naturally arose. Tyndall himself believed that the purely gaseous portion of the atmosphere was incompetent to scatter light and most of the early investigators agreed with him in presuming that the suspended particles were composed of some kind of foreign matter other than the molecules that constitute the atmosphere proper. It was Lord

of the mixture is kept at about 10 mm. On the passage of light, chemical action ensues and a very fine cloud of solid particles begins to form. Another method of preparing an artificial atmosphere consisting of fine particles of sulphur is to add a dilute solution of hydrochloric acid to a very dilute solution of sodium hyposulphite. In this case chemical action takes place without the intervention of light and a cloud of very fine sulphur particles is at first formed. As time goes on, their size gradually increases. The rate of cloud formation can be delicately controlled by varying the concentrations of the solutions, and practically all the important characteristics of the Tyndall phenomenon can easily be demonstrated by this method.

Rayleigh [1] who first pointed out that there were no strong arguments in favour of such an assumption. On the other hand, it is well known that the sky is bluer than ever when the dust and other suspended particles in the atmosphere are washed down by a heavy down pour of rain. The azure is most striking on a clear day or at altitudes above the dust level such as in a hill station. Lord Rayleigh and subsequently Schuster [2] showed that the measured opacity of the atmosphere was in satisfactory agreement with what would be expected if the molecules of the air alone were regarded as the scattering centres. As a result of these investigations, which will be dealt with in greater detail in the following pages, we know to-day that both the blue colour and the luminosity of the sky may be accounted for, without the postulation of any foreign suspended particles.

An equally interesting but a more recondite feature of sky light which may easily be demonstrated with the help of a nicol is its state of partial polarization. No explanation was forthcoming for this phenomenon and it was somewhat puzzling in view of the results obtained in the laboratory by Tyndall with clouds of *small* particles, the light scattered by which exhibited complete polarization in transverse directions. The observed imperfection of polarization of sky light was found to be genuine as it persisted even after eliminating and accounting for the disturbing factors such as dust and other suspended particles in the atmosphere. It could also be reproduced in the laboratory by working with dust-free air. Lord Rayleigh [3] showed that this was due to a lack of spherical symmetry in the optical properties of the molecules. Lord Rayleigh's investigations have thus provided the clue for the explanation of the three most outstanding features that characterize the sky light, namely its colour, intensity and polarization.

Blue of the Ocean.—The remarkable dark blue or indigo colour exhibited by the deep oceanic waters is another familiar sight to every traveller on a sea voyage. Amongst the early

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[1] Scientific Papers, *4*, 397 (1899).
[2] *Optics*, 2nd edition, 328 (1909).
[3] Scientific Papers, *6*, 540 (1918).

attempts to explain this phenomenon, we may again mention that of Lord Rayleigh.[1] He was of the opinion that three different causes, namely, the reflection of the blue sky, the natural hue of the waters arising from dissolved colouring matter and the blue tinge that would be acquired by the light in the process of diffusion by the suspended particles, were operative, thus complicating the issue to a certain extent. While proposing such an explanation, he himself had noticed that the blue of the deep sea often looked purer and fuller than that of the sky. This circumstance is obviously not in favour of the idea that the ocean receives its colour only by reflection. The other two suggestions may easily be shown to be untenable. Colour due to the absorption by the dissolved materials can be expected to manifest itself only by transmitted light which is excluded by the very nature of observation as the observer is always situated in such a position that the transmitted light cannot reach him directly. It is, however, possible that some transmitted light is reflected backwards to the observer by suspended particles but the known great transparency and freedom from turbidity of the many oceanic waters, particularly those that show the blue colour best, precludes the possibility of such an explanation being valid. These and other objections to the above explanation of the blue of the ocean were first raised by Raman.[2] He carried out a number of experiments both on the deck of a steamer and in the laboratory with waters collected from different seas with a view to determine the extent to which the suspended particles were responsible for the colour. As a result of these experiments, he came to the conclusion that light molecularly scattered in the oceanic waters plays a large part in making them look blue, although other complicating factors such as the absorption of red and yellow regions of the spectrum in the water have also to be taken into account in explaining the subsidiary features. This recognition by Raman of the fact that the blue of the oceanic waters is another natural optical phenomenon which presents a close analogy to the

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[1] Scientific Papers, *5*, 540 (1910).

[2] Nature, *108*, 367 (1921) and *Molecular Diffraction of Light* (1922).

blue of the sky may be regarded as an important step in the history of the subject.

Colour of Ice.—Thick layers of ice illuminated by sun-light when viewed transversely show a strikingly blue tinge. The blue colour of ice in glaciers is an example of this phenomenon. Large blocks of ice, carefully selected such that they do not contain any inclusions may be used in the laboratory to demonstrate the effect.

CHAPTER II

LIGHT SCATTERING AS A RESIDUAL EFFECT

Scattering of Light by a Small Dielectric Sphere.—We will now consider the case of a small spherical volume V having a dielectric constant $\varepsilon + \Delta\varepsilon$ embedded in an otherwise uniform medium possessing a dielectric constant ε. If a beam of light of electric intensity E is incident and goes past the obstacle, we have equations (1) and (2) outside the obstacle and within the obstacle respectively.

$$D = \varepsilon E \qquad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

$$D' = (\varepsilon + \Delta\varepsilon)\, E \qquad \ldots \quad \ldots \quad \ldots \quad (2)$$

Equation (2) may be written as (2*a*).

$$D' = \varepsilon\left(1 + \frac{\Delta\varepsilon}{\varepsilon}\right) E \quad \ldots \quad \ldots \quad \ldots \quad (2a)$$

(2*a*) is the same as the original equation (1) if we regard E as having been replaced by $E\left(1 + \frac{\Delta\varepsilon}{\varepsilon}\right)$. The presence of the obstacle has therefore the same effect as the creation of a secondary electric intensity $\frac{\Delta\varepsilon}{\varepsilon}$ E per unit volume at its centre, the direction of the secondary disturbance being the same as that of the original one. If the dimensions of the volume element are small in comparison with the wave-length of light, the aggregate electric intensity will be $\frac{\Delta\varepsilon}{\varepsilon} EV$. Radiation will be emitted in all directions, the laws governing the distribution of which are the same as those that are appropriate to a vibrating electric doublet. It is easy to see that the light emitted in a transverse direction will be linearly polarized if the incident light is linearly polarized and that its intensity will be proportional to $\left(\frac{\Delta\varepsilon}{\varepsilon}\right)^2 E^2V^2$.

Scattering of Light by a Perfectly Homogeneous Medium.—

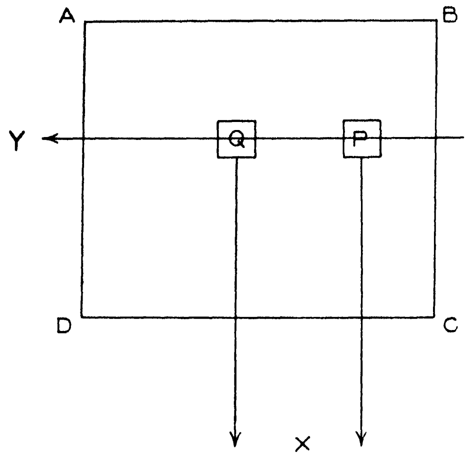


FIG. 1.

Let ABCD represent a block of perfectly homogeneous matter illuminated by light incident in the direction of the Y axis. The whole volume may be divided into a large number of cubes as shown in the figure. The side of each cube is so chosen that it is small in comparison with the wave-length of light. Under such conditions it is easily seen that the phases of all the beams scattered by the different portions of any one cube in a given direction, say X, are in agreement with each other. We may therefore represent the aggregate effect from a particular cube P by $A \cos \frac{2\pi ct}{\lambda}$ where A is the sum of all the amplitudes arising from different portions. If the material is perfectly homogeneous [1] and possesses uniform density at all points, it is always possible to pick out another cube Q at the requisite distance

[1] The conditions prevailing in ordinary crystals closely approach this ideal at low temperatures. The distances between one molecule and its neighbours are so small in comparison with the wave-length of light in the visible region that we may disregard the structure altogether and regard the medium as continuous and if thermal motions are eliminated, every bit will be identical with every other bit at all events.

such that the phase of the light scattered by the latter in the direction X lags behind that coming from the cube P by an amount equal to $\frac{\lambda}{2}$. The corresponding aggregate disturbance may then be written as $A \cos \frac{2\pi}{\lambda}\left(ct - \frac{\lambda}{2}\right)$ and the two will destroy each other. In this manner, all the secondary amplitudes coming from the various cubes may be paired off and shown to leave no aggregate residual effect in the direction of X.[1] The proof may easily be extended to all other directions except the direction along which the light is originally incident. It is well to recall the principal assumptions on which such a conclusion rests. They are:—

(i) The material may be regarded as perfectly homogeneous and divided into a number of cubes each of which is small in comparison with the wave-length of light. Such a division should not result in bringing out the structural discontinuity, if any, into prominence.

(ii) Any one cube is similar in all respects to every other cube at all instants of time.

(iii) Consequently, for any given cube we are quite certain of finding another at the requisite distance such that the secondary rays that are emitted in a given direction by these two cubes completely destroy each other.

Fluctuations as the Cause of Light Scattering.—From what has been said in the foregoing sections of this chapter, it is easily seen that although an individual dielectric sphere may be expected to emit light under the action of an incident light wave as if it were an electric doublet, a perfectly homogeneous medium should not show body scattering. This has been shown to be a consequence of regarding the medium as made up of a number of identical volume elements, the compounded effect from all of which reduces to nothing. Similar considerations may easily be shown to apply to the case of a large number of small dielectric

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[1] This does not apply to the cubes near the boundaries.

spheres embedded at regular intervals in a medium of otherwise uniform dielectric constant. This case corresponds to an actual crystal in which thermal motions are ignored and the molecules are regarded as spherical dielectric particles. The particles are small in comparison with the wave-length of light in the visible region and are so close to each other that the medium may be regarded as structureless and it follows as before that there is no residual effect left in a lateral direction if all the amplitudes are compounded. We may alternatively look at it by considering the effect from each dielectric sphere. If a particular sphere causes a certain disturbance at the observer, it is always possible to discover another sphere, since they are all arranged in a regular fashion and are devoid of thermal motions, which will cause a disturbance which differs in phase from the former one by such an amount as to cause complete destructive interference. In this way the aggregate effect may be seen to reduce to nothing, as the amplitudes from suitable pairs cancel each other. Why then is there a finite scattering in a lateral direction?

Thermal motions cannot obviously be neglected. The dielectric spheres are moving hither and thither about their equilibrium positions and these movements cause a certain amount of fluctuation in the physical properties of the small volume elements about their mean values. This element of chaos results in a residual effect being left over as it may easily be shown that complete destructive interference is then not possible. In the continuum picture, this is equivalent to saying that the two volume elements which are expected to annul each other's effects need not be identical at a given instant of time and thus completely cancel each other's effects. In the latter picture, where the medium is regarded as composed of a large number of dielectric spheres, this is equivalent to saying that for every sphere there is not the absolute certainty of finding another exactly at the required distance as they have been given a certain amount of freedom of movement. The result is that such fluctuations cause a residual amplitude to be left over and light is emitted in a lateral direction. With increasing fluctuations of this type, the intensity of the residual effect increases. If the motions of the dielectric spheres become

more and more chaotic or more and more uncorrelated with each other, the fluctuations become increasingly prominent and the scattered light gains in intensity. This is the general explanation of the fact that, molecule per molecule, a gas usually scatters light more intensely than a liquid and the latter more intensely than a solid. Scattering of light is thus essentially a fluctuation phenomenon.

Chapter III

LAWS OF SCATTERING OF LIGHT

1. *Scattering by an Isolated Molecule treated as a Dielectric Sphere.*—We have seen that a dielectric sphere, under the action of an incident oscillating electric field E, may be replaced by an oscillating electric intensity $\frac{\Delta\varepsilon}{\varepsilon}$ EV for purposes of calculating the secondary radiation that is emitted by it. ε may be regarded as equal to unity if the particle is embedded in vacuum and it is easily seen that $\frac{\Delta\varepsilon \,.\, EV}{4\pi}$ will then represent the electric moment induced in an isolated molecule by the incident electric field. $\frac{\Delta\varepsilon \,.\, V}{4\pi}$ may be denoted by α and termed the polarizability of the molecule. αE is an oscillating electric moment and its maximum value will be αE_0 if $E = E_0 \cos 2\pi\nu t$. If we regard E as being confined to the direction OZ (see Fig. i of Appendix I) and the light is taken as incident in the direction OY, we obtain the expression for the mean rate of radiation from the molecule in a direction transverse to that of the incident light by putting $e^2E_0^2 = E_0^2\alpha^2$ and $\theta = 90°$ in equation (3) of Appendix I, as

$$\frac{(2\pi\nu)^4}{8\pi c^3 r^2} E_0^2\alpha^2. \quad .. \quad .. \quad .. \quad (1)$$

The average energy contained in the incident light wave of amplitude E_0 is however equal to $\frac{c}{8\pi} \,.\, E_0^2$. The radiation scattered by each molecule in a transverse direction when expressed as a fraction of the incident energy is therefore given by

$$\left(\frac{2\pi}{\lambda}\right)^4 . \frac{1}{r^2} . \alpha^2. \quad .. \quad .. \quad .. \quad (2)$$

The scattered radiation is polarized with the vibrations confined to the direction along which the incident electric intensity itself

acts. The corresponding amplitude may be written as

$$\frac{4\pi^2}{\lambda^2 r} \cdot p, \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (3)$$

where p is the actual moment induced by the incident electric field. Similarly, it may be seen from (4) of Appendix I, that the total energy scattered by each molecule is

$$\frac{\omega^4}{3c^3} \cdot E_0{}^2 \alpha^2. \quad \ldots \quad \ldots \quad \ldots \quad (4)$$

After substituting $\frac{2\pi c}{\lambda}$ for ω, this may be expressed as a fraction of the incident energy as

$$\frac{128\pi^5}{3\lambda^4} \cdot \alpha^2. \quad \ldots \quad \ldots \quad \ldots \quad (5)$$

It is easily seen from equation (2) of Appendix I, that in the direction OZ ($\theta=0$) the intensity of scattering is zero and as we proceed from OZ to OX, the intensity gradually increases to its maximum value given by (1). In the XY plane, the intensity is always given by (1) and is therefore independent of the obliquity of observation. If we use an incident unpolarized beam, it may be regarded as consisting of two independent vibrations, one along OZ and the other along OX each having an amplitude E_0. The aggregate effect in the direction of OX will still be given by (1) and the scattered light will be polarized completely, the vibrations being confined to OZ since the moment induced parallel to OX will not produce any effect in the direction OX. The incident energy is now twice that in the previous case and hence the radiation scattered by each molecule in a transverse direction when expressed as a fraction of the incident energy will be only $\frac{8\pi^4}{\lambda^4} \cdot \frac{1}{r^2} \cdot \alpha^2$ instead of the expression given by (2). On the other hand, in an oblique direction making an angle β with the course of the incident light, the moment induced in the direction OX will give a component which is $\cos^2\beta$ times the component arising from OZ. Thus we have for the total intensity in the oblique direction

$$(1+\cos^2\beta)\,\frac{8\pi^4}{\lambda^4} \cdot \frac{1}{r^2} \cdot \alpha^2. \quad \ldots \quad \ldots \quad \ldots \quad (6)$$

It may be noted that the intensity in either the backward or nearly forward directions is twice that obtained in the transverse direction.

The state of polarization is perfect in the transverse direction, the intensity of the horizontal component being zero. The polarization of the scattered light gradually becomes imperfect till it attains the maximum imperfection (a state in which the intensity of the horizontal component is equal to the intensity of the vertical component) in the backward direction. If we define ρ, the depolarization of the scattered light, as the ratio of the intensity of the horizontal component to that of the vertical component, we can easily see that its value in any direction OX′ (Fig. i of Appendix I) will be given by

$$\rho_{ox'} = \cos^2\beta. \quad .. \quad .. \quad .. \quad (7)$$

Equations (6) and (7) are the essential consequences of the theory outlined above. The outstanding results implied in these equations are given below as items 1, 2 and 3 :—

1. The intensity of scattering is proportional to the square of the polarizability of the molecule.
2. The intensity of the scattered light varies inversely as the fourth power of the wave-length, if we neglect the small dependence, if any, of the polarizability on the wave-length.
3. Light scattered in a direction strictly transverse to the direction of propagation of the incident beam exhibits complete polarization irrespective of whether polarized or unpolarized incident light is used.

A Gaseous Assembly of Molecules.—In the foregoing section, theoretical expressions were derived only for the case of a single molecule. In the present section, it will be shown that the essential conclusions are not altered at all when the theory is extended to an assembly of gaseous molecules. It has already been remarked that the individual molecules through which the primary waves pass are to be regarded as secondary sources of radiation. If the molecules are arranged in a regular order and if they stick absolutely to their positions, the individual

effects may easily be compounded. The matter is, however, not so simple when we come to consider the various secondary waves starting from the different molecules of a gas. The question of the existence or otherwise of a definite phase relationship between these secondary waves has been discussed at length by Rayleigh,[1] Larmor[2] and Raman[3]. In the case of a rarefied gas, we may regard the molecules as randomly distributed, the actual volume of the matter itself being a very small fraction of the total space occupied by the gas. These are precisely the conditions for the gas being termed *ideal* or for its conforming to Boyle's law. It is obvious that the scattering centres are then spaced widely enough in relation to the wave-length of light so as to act as independent sources. Lord Rayleigh has shown that under such conditions, the *expectation*[4] of intensity in any direction is n times that due to a single centre, where n is the total number of centres. In such cases or in cases which approximate closely to this ideal, all the intensity expressions and polarization rules derived in the foregoing section for a single molecule continue to be valid.

In this connection, we have to deal with the special case of scattering in the forward direction separately and consider it in greater detail. In such a case, a given layer, which is at right angles to the direction of propagation of the incident light, may be divided into a number of zones. The phase relationship that exists between the radiations emitted by the different molecules, lying in different zones, may easily be ascertained. To take a concrete example, consider a wave front meeting two molecules A and B belonging to a particular zone, the direction of propagation being Y′Y (Fig. 2).

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[1] Scientific Papers, *3*, 47 (1888) and *6*, 565 (1918).

[2] Phil. Mag., *37*, 161 (1919).

[3] *Molecular Diffraction of Light* (1922).

[4] The word *expectation* here stands for what we should expect as a mean of all the results obtained in a large number of trials. This does not at all imply that in any single trial, the result will be n times that obtained with one molecule.

The incident wave that meets B is in advance of phase with respect to that which meets A. As a consequence, the secondary

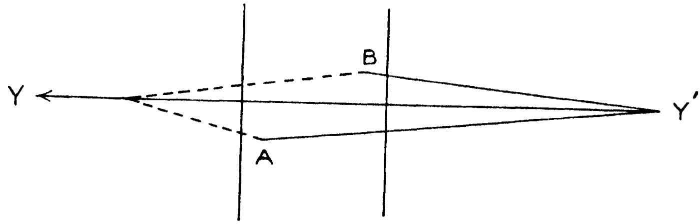


FIG. 2.

wave that is emitted by B is in advance of phase to the same extent in relation to the secondary wave emitted by A. In the forward direction, the wave starting from B would have had to travel a greater distance and suffer just the requisite amount of retardation so as to compensate for the advancement of phase which it had initially acquired. In this manner, we can easily show that so far as the forward direction or directions extremely close to it are concerned, the secondary waves starting from molecules in a given zone are all optically coherent. This result is unaffected by the closeness of packing of the molecules in the layer under question.

In other directions, however, owing to the fact that the molecules are distributed at random in the gas, no such exact compensation of phase differences as would occur in the forward direction is possible. As a consequence of this special feature in the forward direction, in order to find the resultant effect, we are obliged to add up the amplitudes of the different secondary radiations and compound the result with the amplitude of the incident wave. Such a procedure results in a retardation of phase which may be identified with the refractivity of the medium and thus an important relationship between the refractivity and the scattering power of the medium may be deduced.

The results 1, 2, 3 of the foregoing section were first deduced by Lord Rayleigh.[1] He also made an experimental comparison of these conclusions with the actual state of affairs regarding

[1] Scientific Papers, *1*, 87 (1871).

the composition and state of polarization of sky light. Sky light, taken from the neighbourhood of the zenith, was compared with the direct sun-light diffused through a white paper and the figures given in the following Table were obtained. The results calculated from (5) on the basis of a standard intensity for the incident light at different wave-lengths are also given for comparison.

Spectral Region..	C	D	b_3	F
Calculated ..	25	40	63	80
Observed ..	25	41	71	90

The two sets of numbers are made to agree at C and the agreement between the calculated and observed values at other wave-lengths is very significant as it shows that the sky light is subject to the inverse fourth power law. It is therefore presumably due to scattering by the molecules of the atmosphere.

The variation of intensity in the scattered beam, implied in the above theory and similary calculated, is also represented diagrammatically in Fig. 3, taking the scattered light at λ4000 as 100. The preponderance of the blue and the rapid diminution in intensity of the longer wave-lengths in the scattered light is most striking.

The relatively feeble intensity of the longer wave-lengths in the diffuse sky light, which is a consequence of the Rayleigh fourth power law, is taken advantage of in several instances of practical importance. Photographs of landscape or other objects which are illuminated by direct sun-light will exhibit a striking contrast against the background of the sky if a filter transmitting only the longer wave-lengths is used in the process. Wood[1] obtained some of the earliest pictures of this type using a filter consisting of a tank of dense cobalt glass filled with a solution of bichromate of potash, which transmits the region between λ6900 and 7400. 'In these photographs the foliage appeared snow-white against a coal-black sky, and

[1] A very striking photograph of this kind is reproduced in *Physical Optics* (1934).

distant mountains, completely obscured by haze in ordinary photographs came out clearly.'

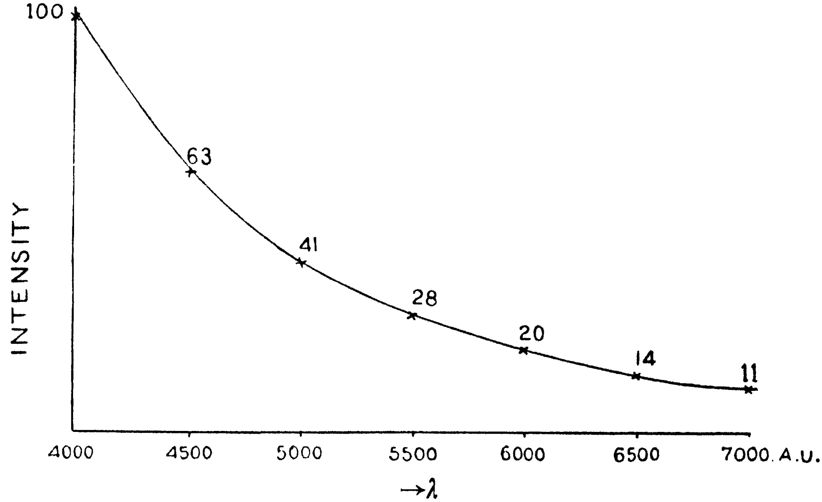


FIG. 3.

Relation between the Scattering Power, the Refractive Index and the Attenuation Coefficient.—It has already been mentioned that the compounding of the secondary waves, scattered in the forward direction, with the primary beam results in a retardation of phase which may be interpreted as refraction. Moreover, the transmitted beam should lose energy which is equal to that radiated by the molecules of the medium as scattered light. This loss is frequently referred to as attenuation in order to distinguish it from ordinary absorption. It is evident that these three phenomena, namely refraction, attenuation and light scattering must be closely connected with each other. First of all, we will calculate the damping term appropriate to the attenuation caused by secondary radiation by assuming that the rate at which the energy of the vibrating dipole is decreasing is equal to the rate at which it is radiating energy. We will then use the result to obtain the relation between attenuation and refraction.

Let a plane polarized light wave $E = E_0\cos 2\pi\nu t$ be incident in the direction OY on a molecule. The electric vector is assumed to be parallel to OZ (Fig. i of Appendix I). An oscillating moment, whose maximum value is given by Ze where Z is the amplitude of the vibrating electron, will be induced in the molecule. The appropriate expressions for the amount of radiation scattered by such a dipole and for the corresponding attenuation suffered by the incident beam as it goes past the molecule, may easily be obtained by studying the equation of motion of the electron. In forming the equation of motion, besides the sinusoidal external electric force $E_0\cos 2\pi\nu t$ and the elastic restoring force, we introduce a damping force proportional to the velocity at each instant to account for attenuation.[1] This damping term is analogous to the one used for explaining light absorption but is different from it and may be termed the radiation resistance. The exact magnitude of the damping force may be calculated on the assumption that the rate at which the energy of the vibrating dipole is decreasing is equal to the rate at which it is radiating energy. The equation of motion may be written as

$$m\ddot{z}+mb\dot{z}+\omega_0^2mz = eE_0e^{i\omega t}. \qquad \ldots \qquad \ldots \quad (8)$$

The real part of $E_0e^{i\omega t}$ represents the electric force. m is the mass of the electron and ω stands for $2\pi\nu$. ω_0 is the natural frequency of the electron and thus enters the term for the elastic restoring force. As a solution of the above equation, we have

$$Z = \frac{\frac{e}{m}E_0e^{i\omega t}}{\omega_0^2-\omega^2+i\omega b} \cdot \ldots \qquad \ldots \qquad \ldots \quad (9)$$

Thus the electron is thrown into forced vibration, the frequency being the same as that of the incident light wave and the displacement being confined to the direction of the electric vector in the incident light wave. The dipole moment is of an

[1] Ordinarily, a damping term is introduced to account for light absorption. This is of significance only when we are in the neighbourhood of an absorption band but may not be considered if we are dealing with regions far removed from absorption bands.

oscillating type and has a value given by

$$Ze = \frac{\frac{e^2}{m} E_0 e^{i\omega t}}{\omega_0^2 - \omega^2 + i\omega b}. \quad \quad (10)$$

The vibrating dipole emits radiation which is of the same frequency as the incident light. The intensity of the emitted radiation in different directions will be governed by expression (3) of Appendix I. An important fact to be noticed is that the amplitude Z of the dipole is less than E_0, the amplitude of the incident light wave. In the foregoing, it has been assumed for simplicity that the molecule under consideration contains only one electron but the statements are quite general and apply even to the case of molecules having a larger number of electrons, all having either identical or different natural frequencies. In order to obtain the dipole moment of each molecule, the right hand side of (10) has merely to be summed up over all the electrons. The maximum value of this moment may be written as $E_0\alpha$, where

$$\alpha = \frac{\frac{e^2}{m}}{\omega_0^2 - \omega^2 + i\omega b} \quad \quad (11)$$

α has already been called the polarizability of the molecule and we see that it is a function of the frequency of the incident light. If ω is very small in comparison with ω_0, i.e., if we are dealing with regions far on the longer wave-length side of the natural frequency of the electron, α does not sensibly depend upon the incident frequency and is nearly equal to $\frac{e^2}{\omega_0^2 m}$. The latter is the limiting value of the above function and is obtained at zero frequency or a static field.

The equation of motion of the electron is given by (8). By solving this equation, we obtain (9) for the displacement of the electron. The real part of (9), which may be written as $\frac{\frac{e}{m} E_0 \cos\omega t}{\omega_0^2 - \omega^2}$, if the damping is small, represents the actual

displacement. Therefore, the velocity at any instant is given by $\dfrac{\dfrac{-e\omega}{m}E_0\sin\omega t}{\omega_0^2-\omega^2}$. The rate of work done against the damping force is found by evaluating $mb\dot{z}\times\dot{z}$ as follows.

$$mb\dot{z}\times\dot{z} = \frac{be^2\omega^2E_0^2\sin^2\omega t}{m(\omega_0^2-\omega^2)^2}.$$

The time average of this may be written as $\dfrac{be^2\omega^2E_0^2}{2m(\omega_0^2-\omega^2)^2}$. The rate at which the vibrating dipole is radiating energy is given by (see 4 and 11)

$$\frac{\omega^4}{3c^3}\cdot\frac{e^4}{m^2}\cdot\frac{E_0^2}{(\omega_0^2-\omega^2)^2},$$

after neglecting $i\omega b$ in the denominator for α. Equating these two, we have for b

$$b = \frac{2\omega^2e^2}{3c^3m}.$$

After substituting $\dfrac{2\pi c}{\lambda}$ for ω, we obtain

$$\omega b = \frac{16\pi^3}{3\lambda^3}\cdot\frac{e^2}{m}. \qquad \text{(12)}$$

Using the above value of radiation damping, we can now obtain a relationship between attenuation and refraction. The passage of a light wave along the Y axis through a non-absorbing medium may be represented by the equation

$$E' = E_0e^{-ky}e^{\frac{2\pi i}{\lambda}(ct-ny)}. \qquad \text{(13)}$$

At the origin ($y=0$), the displacement is that of the original light wave and is in the Z direction. It is given by $E=E_0e^{2\pi i\nu t}$. The term e^{-ky} represents a diminution in the amplitude as the wave is passing and therefore corresponds to attenuation. The second exponential merely represents a retardation of phase corresponding to a refractive index n. Equation (13) may be rewritten as

$$E' = E_0e^{\frac{2\pi i}{\lambda}\left\{ct-y(n-ik')\right\}}, \text{ where } k' = \frac{k\lambda}{2\pi}.$$

Thus the phenomena accompanying the passage of the wave may be completely accounted for by assuming a complex refractive index equal to $n-ik'$. Such a complex refractive index implies a certain relationship between n and k' which may be deduced as follows. The complex refractive index may also be evaluated from the dipole moment induced in each molecule. Using (10), we obtain the following expression for P, the moment induced per unit volume.

$$P = \sum_{\nu} ze = \frac{\nu \cdot \frac{e^2}{m} \cdot E_0 e^{i\omega t}}{\omega_0{}^2 - \omega^2 + i\omega b}.$$

ν is the number of molecules per cubic centimeter of the medium which is supposed gaseous.[1] The displacement vector D is obtained as

$$D = E + 4\pi P = E\left(1 + 4\pi \cdot \frac{\frac{\nu e^2}{m}}{\omega_0{}^2 - \omega^2 + i\omega b}\right).$$

Dividing throughout by E, we have

$$\frac{D}{E} = (n-ik')^2 = 1 + 4\pi \cdot \frac{\frac{\nu e^2}{m}}{\omega_0{}^2 - \omega^2 + i\omega b}.$$

Since n is nearly unity for gases, we have as an approximation

$$n - ik' = 1 + 2\pi \cdot \frac{e^2}{m} \cdot \frac{\nu}{\omega_0{}^2 - \omega^2 + i\omega b}.$$

Separating the real and imaginary parts, we have

$$n = 1 + 2\pi \cdot \frac{e^2 \nu}{m} \cdot \frac{\omega_0{}^2 - \omega^2}{(\omega_0{}^2 - \omega^2)^2 + \omega^2 b^2} \quad .. \quad (14)$$

$$k' = 2\pi \cdot \frac{e^2 \nu}{m} \cdot \frac{\omega b}{(\omega_0{}^2 - \omega^2)^2 + \omega^2 b^2}. \quad .. \quad .. \quad (15)$$

If we neglect $\omega^2 b^2$ and retain only ωb in the above expression, it may be written, after adopting the value of ωb from (12), as

$$k' = 2\pi \cdot \frac{e^2 \nu}{m} \cdot \frac{16\pi^3}{3\lambda^3} \cdot \frac{e^2}{m} \cdot \frac{1}{(\omega_0{}^2 - \omega^2)^2}.$$

[1] ν also stands for the frequency, but there is not likely to be any confusion.

Combining this with (14), we obtain

$$k' = \frac{8\pi^2}{3\nu\lambda^3} \cdot (n-1)^2 \quad \text{or } k = \frac{16\pi^3(n-1)^2}{3\nu\lambda^4}.$$

This tells us that apart from a change of phase in accordance with the second term of (13), the amplitude of the light wave is suffering an attenuation in accordance with the first term on account of the scattered radiation, the attenuation being given by the relation

$$E' = Ee^{-ky}, \quad \text{where } k = \frac{16\pi^3(n-1)^2}{3\nu\lambda^4}.$$

Squaring both sides, we may write

$$I' = Ie^{-hy} \quad \text{where } h = 2k.$$

h is called the attenuation coefficient and is given by the relation

$$h = \frac{32\pi^3 (n-1)^2}{3\nu\lambda^4}.$$

It may easily be seen from (5), after substituting $\frac{n^2-1}{4\pi\nu}$ for α, that this also represents the total amount of energy scattered away per unit volume of the medium. This important relationship, showing the connection between the attenuation coefficient or the energy scattered by a layer of gas consisting of spherically symmetrical molecules and its refractive index, was first deduced by Lord Rayleigh [1] in a slightly different manner. A complete discussion of this aspect of the subject has also been given by Lorentz.[2]

✓ *Disagreement between Experiment and Theory in Respect of Perfect Polarization.*—If the view that the light of the sky consists largely of sun-light scattered by the atmosphere in accordance with the laws of molecular scattering, deduced in the foregoing, is correct, we should expect that besides exhibiting a blue colour, it should be perfectly polarized in directions transverse to the incident sun-light. Repeated and careful observations have, however, shown that there is a considerable imperfection of polarization in the light of the sky even when observations are made in the transverse direction. Much of this imperfection

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[1] Scientific Papers, *4*, 397 (1899).

[2] Collected Papers, *3*, 239 (1910).

may be attributed to disturbing factors such as dust, thin clouds or haze and the fact that the light illuminating the atmosphere is not merely the direct light of the sun, but also the light diffused from the sky and from the earth's surface, etc. In the case of sky light itself, it is no doubt very difficult to eliminate all these factors in practice but the very careful and pioneering observations of Lord Rayleigh[1] on a laboratory scale showed that light scattered in a transverse direction by dust-free air was far from being completely polarized. A perpendicular component whose intensity was about 4% of the parallel component was definitely observed and photographed. Even in the case of sky light, it has been found possible to obtain a reasonable estimate of the genuine part of depolarization by making observations at higher altitudes and on bright and clear days thus eliminating the complicating features to a large extent. The effect of secondary scattering has been considerably reduced by confining the observations to long wave-lengths such as are transmitted through a red glass. The effect of light reflected from the earth's surface is corrected for, by utilizing the data available on the albedo of different types of landscape. Raman made observations on these lines at a height of 8,750 feet above the sea level and concluded that out of an observed depolarization of 13%, a sum total of 9% should be ascribed to the earthshine and secondary scattering, thus leaving a residual depolarization of about 4% to be still accounted for. This residual depolarization is presumably of a molecular origin and is in good agreement with the observations made by Lord Rayleigh in the laboratory.

Such an imperfection of polarization in the molecularly scattered light is by no means a consequence of the simple theory outlined in the foregoing pages. We should, on the other hand, expect to find perfect polarization. It is thus obvious that the theory as outlined so far is incomplete in some important respects. We now know that the explanation of this genuine depolarization of scattered light lies in the fact that the molecules, which are the real scattering centres in the atmosphere on a

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[1] Proc. Roy. Soc., *94*, 453 (1918) and *95*, 155 (1918).

clear day, are not spherical but are to be regarded in general as asymmetric. The simple theory of Lord Rayleigh has therefore to be adapted to the case of scattering by molecules which do not possess spherical symmetry.

Anisotropy of Molecules.—The phenomenon of light scattering may hereafter be pictured as a consequence of the incident light wave inducing an oscillating electric moment in a molecule which is optically unsymmetrical. The magnitude of this induced moment will be a measure of both the refractive index of the medium and its scattering power. We may write the equation

$$p = \alpha E$$

where p is the moment induced, α the polarizability of the molecule and E the incident electric vector. It is correct to assume that α is independent of direction only in the case of spherically symmetrical molecules. In a general case, α will naturally be a function of direction and has to be regarded as a tensor of the second order. There will be three principal axes fixed in the molecule in respect of which equations of the type $p_{x'} = AE_{x'}$ etc., hold good. This is a consequence of the fact that when the tensor components are expressed in this co-ordinate system, all the non-diagonal terms vanish. The diagonal terms that are retained may be denoted by A, B and C and termed the principal polarizabilities of the molecule. It is easily seen that when an incident light vector acts on the molecule along any of these principal directions alone, is the induced moment parallel to the incident vibration. In the general case, however, the incident vibration vector, does not coincide with the induced moment vector, with the result that a molecule under the influence of an incident plane polarized beam will scatter light having its direction of vibration slightly inclined to the original vibration vector. The scattered beam, under these conditions, will obviously exhibit a weak component in a direction perpendicular to the direction of vibration in the incident beam. Molecules, differently oriented with respect to the incident vibration, will give weak components of different magnitudes and the aggregate effect is evidently the cause of the observed depolarization of the molecularly scattered light. If

the molecule is spherically symmetrical, the orientation does not matter at all and the induced moment and therefore the vibration in the scattered ray is always parallel to the incident disturbance. We will now treat the case of an asymmetric molecule in detail.

Depolarization of Light Scattered by Anisotropic Molecules.— We will at first deal with a simple case as this will again be referred to in the subsequent chapters and then pass on to the general case. Moreover, the treatment in this case being much simpler, will prepare the ground for the more elaborate one. Let the molecules under consideration possess an axis of rotational symmetry such that their polarizability ellipsoids are spheroids ($A = B \neq C$). Let the principal axes of the polarizability ellipsoid, denoted by dashed letters, cut the surface of a sphere at X', Y' and Z' for a particular position θ, φ of the molecule. The sphere is of unit radius and is drawn with O, the origin of the co-ordinate systems, as centre (Fig. 4). Z' is the axis of symmetry ($A = B$) and we can regard that the principal axes in this plane are represented by X' and Y' without

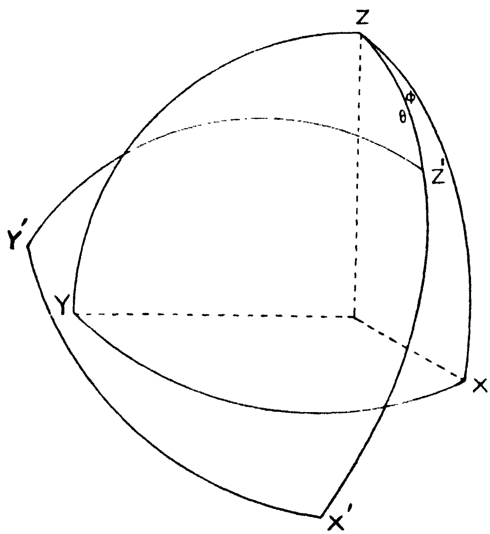


FIG. 4.

any loss of generality. The following table gives the cosines of the various angles.

	X	Y	Z
X′	$\cos\theta \cos\varphi$	$\cos\theta \sin\varphi$	$-\sin\theta$
Y′	$-\sin\varphi$	$\cos\varphi$	0
Z′	$\sin\theta \cos\varphi$	$\sin\theta \sin\varphi$	$\cos\theta$

If the tensor components referred to the space fixed co-ordinate system are denoted by α_{xy}, their values for the particular position of the molecule are given by the set of equations (16).

$$\alpha_{xy} = \sum_{x'y'} \alpha_{xy}' \cos XX' \cos YY'. \quad .. \quad .. \quad (16)$$

The coefficients α_{xy}' relate to the case where X Y Z coincide with X′ Y′ Z′ and so we have

$$\alpha_{xy}' = \alpha_{yz}' = \alpha_{zx}' = 0\,;\ \alpha_{zz}' = C\,;\ \alpha_{xx}' = \alpha_{yy}' = A.$$

Since α is to be regarded as a symmetric tensor, no distinction need be made between terms like α_{xy} and α_{yx} or α_{xz} and α_{zx} etc. With the help of these relations and the Table of cosines, we can easily evaluate all the tensor components in (16). The components of p in terms of α_{xy} are given by (17)

$$p_x = \sum_{y} \alpha_{xy} E_y \quad .. \quad .. \quad .. \quad (17)$$

and analogous equations for p_y and p_z. In the special case where the vibrations in the incident electric vector are confined to the Z axis alone (plane polarized light incident along the OY axis), we have

$$p_z = \alpha_{zz} E_z = (C \cos^2\theta + A \sin^2\theta) E_z$$

$$p_y = \alpha_{yz} E_z = (C - A) \sin\theta \cos\theta \sin\varphi \,.\, E_z.$$

p_y will obviously not exist if A and C are equal. If the scattered light is observed in the direction OX, p_z^2 will be a measure of

the intensity[1] of that part of the scattered light arising from a molecule θ, φ and polarized in the direction OZ, i.e., parallel to the incident vibrations. p_y^2, on the other hand, will give the intensity of the part which is polarized in the direction OY, i.e., perpendicular to the incident vibrations. Any moment induced parallel to the direction OX will produce no intensity of scattering in the direction OX. It must, however, be remembered that in a volume of gas, there are molecules randomly oriented with all possible values of θ and φ thus giving rise to varying values of p_z and p_y. The average intensity per molecule in such a case will be obtained by dividing the aggregate intensity by the total number of molecules. Denoting these averages by $\overline{p_z^2}$ and $\overline{p_y^2}$, we have

$$\overline{p_z^2} = \frac{\int_0^\pi \int_0^{2\pi} E_z^2 (C\cos^2\theta + A\sin^2\theta)^2 \sin\theta\, d\theta d\varphi}{\int_0^\pi \int_0^{2\pi} \sin\theta\, d\theta d\varphi}$$

$$= \frac{E_z^2}{15}(3C^2+8A^2+4AC)$$

$$\overline{p_y^2} = \frac{\int_0^\pi \int_0^{2\pi} E_z^2 (C-A)^2 \sin^2\theta \cos^2\theta \sin^2\varphi \,.\, \sin\theta\, d\theta d\varphi}{\int_0^\pi \int_0^{2\pi} \sin\theta\, d\theta d\varphi}$$

$$= \frac{E_z^2}{15}(C-A)^2.$$

The depolarization ϱ_v of the scattered light in the transverse direction will therefore be

$$\varrho_v = \frac{\overline{p_y^2}}{\overline{p_z^2}} = \frac{(C-A)^2}{3C^2+8A^2+4AC} \quad \ldots \quad \ldots \quad (18)$$

If unpolarized incident light is used, it may be regarded as consisting of an electric intensity E_x in the direction OX in

[1] The actual intensity will be only proportional to p_z^2 but the constant will be omitted for the sake of brevity.

addition to the electric intensity E_z in the direction OZ, each of them being equal to E. It is easily seen that the effect of such an alteration will be merely to add a term equal to $(C-A)^2$ to both the numerator and denominator in (18). The depolarization ϱ_u will be given by [1]

$$\varrho_u = \frac{2(C-A)^2}{4C^2+9A^2+2AC}. \qquad \qquad (19)$$

It may be noticed that in the process adopted for obtaining the aggregate effect, we have summed up the squares of the induced moments. This implies that the secondary waves arising from the different molecules are all optically incoherent. It has already been mentioned that such a procedure is justified and should be adopted only in the case of gases and for oblique directions.

We shall now pass on to the general case. All special cases may be deduced therefrom with suitable modifications. Let

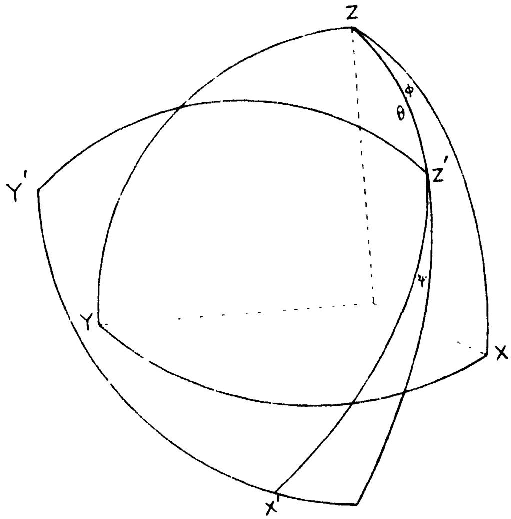


FIG. 5.

[1] The suffix u is used here merely to distinguish this case from the previous one where the incident light was plane polarized with its vibrations taking place in a vertical direction (OZ). Hereafter, the suffix will be dropped and ρ should be taken as referring only to the case of unpolarized incident light unless otherwise specified.

θ, φ, ψ (Fig. 5) determine the orientation of a particular molecule. OX′, OY′ and OZ′ are the principal axes of the polarizability ellipsoid and let the polarizabilities along these directions be represented by A, B and C respectively. OXYZ is the system of rectangular co-ordinates fixed in space. All co-ordinate axes are represented by the points at which they cut the surface of a sphere drawn with O as the centre. The following relationships for the various cosines easily follow.

	X	Y	Z
X′	$\cos\psi \cos\phi \cos\theta - \sin\psi \sin\phi$	$\sin\psi \cos\phi + \cos\psi \sin\phi \cos\theta$	$-\sin\theta \cos\psi$
Y′	$-\sin\psi \cos\phi \cos\theta - \cos\psi \sin\phi$	$\cos\psi \cos\phi - \sin\psi \sin\phi \cos\theta$	$\sin\theta \sin\psi$
Z′	$\sin\theta \cos\phi$	$\sin\theta \sin\phi$	$\cos\theta$

Let E_x, E_y and E_z be the components of the electric intensity E of an incident beam of light, in the directions X, Y and Z respectively. Denoting by p_z, the aggregate component of the induced moment in the direction OZ arising from E_x, E_y and E_z, we have by analogy with (17)

$$p_z = \sum_y \alpha_{zy} E_y.$$

The components α_{zy} may easily be evaluated as before with the help of equation (16) and the Table of cosines given above and p_z explicitly written as

$$\begin{aligned} p_z = & -AE_x \sin\theta \cos\psi (\cos\psi \cos\varphi \cos\theta - \sin\psi \sin\varphi) \\ & -BE_x \sin\theta \sin\psi (\sin\psi \cos\varphi \cos\theta + \cos\psi \sin\varphi) \\ & +CE_x \sin\theta \cos\varphi \cos\theta \\ & -AE_y \sin\theta \cos\psi (\sin\psi \cos\varphi + \cos\psi \sin\varphi \cos\theta) \\ & +BE_y \sin\theta \sin\psi (\cos\psi \cos\varphi - \sin\psi \sin\varphi \cos\theta) \\ & +CE_y \sin\theta \sin\varphi \cos\theta \\ & +AE_z \sin^2\theta \cos^2\psi + BE_z \sin^2\theta \sin^2\psi + CE_z \cos^2\theta. \end{aligned}$$

It may be noted that the following relations hold good in this case.

$$\alpha_{xy}' = \alpha_{yz}' = \alpha_{zx}' = 0 \, ; \; \alpha_{xx}' = A \, ; \; \alpha_{yy}' = B \, ; \; \alpha_{zz}' = C.$$

p_z^2 will be a measure of the intensity of that part of the scattered beam in which the vibrations are restricted to the OZ direction. If there are a large number of randomly oriented molecules and if the light scattered by any one molecule is quite uncorrelated in phase with that scattered by any other, the average intensity per molecule is obtained in the usual way by evaluating the integrals in (20).

$$\overline{p_z^2} = \frac{\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi} p_z^2 \sin\theta \, d\theta d\varphi d\psi}{\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi} \sin\theta \, d\theta d\varphi d\psi} \quad \cdots \quad \cdots \quad (20)$$

The limits of integration are obviously 0 and π for θ and 0 and 2π for φ and ψ. The necessary averages for the trigonometrical functions that occur in the expansion of (20) are given below.

$$\overline{\sin^4\theta} = \tfrac{8}{15},\ \overline{\cos^4\theta} = \tfrac{1}{5},\ \overline{\sin^2\theta} = \tfrac{2}{3},\ \overline{\cos^2\theta} = \tfrac{1}{3},\ \overline{\sin^2\theta\cos^2\theta} = \tfrac{2}{15}$$

$$\overline{\sin^4\varphi} = \overline{\cos^4\varphi} = \overline{\sin^4\psi} = \overline{\cos^4\psi} = \tfrac{3}{8},$$

$$\overline{\sin^2\varphi} = \overline{\cos^2\varphi} = \overline{\sin^2\psi} = \overline{\cos^2\psi} = \tfrac{1}{2},\ \overline{\sin^2\varphi\cos^2\varphi} = \overline{\sin^2\psi\cos^2\psi} = \tfrac{1}{8}.$$

The averages of all odd powers vanish. Expansion and simplification of (20) give (21).

$$\begin{aligned}\overline{p_z^2} &= E_z^2\{\tfrac{1}{5}(A^2+B^2+C^2)+\tfrac{2}{15}(AB+BC+AC)\}\\ &\quad +(E_x^2+E_y^2)\{\tfrac{1}{15}(A^2+B^2+C^2-AB-BC-AC)\}. \quad (21)\end{aligned}$$

It may easily be shown by a similar treatment, or inferred from considerations of symmetry, that

$$\begin{aligned}\overline{p_x^2} &= E_x^2\{\tfrac{1}{5}(A^2+B^2+C^2)+\tfrac{2}{15}(AB+BC+AC)\}\\ &\quad +(E_y^2+E_z^2)\{\tfrac{1}{15}(A^2+B^2+C^2-AB-BC-AC)\} \quad (22)\end{aligned}$$

$$\begin{aligned}\overline{p_y^2} &= E_y^2\{\tfrac{1}{5}(A^2+B^2+C^2)+\tfrac{2}{15}(AB+BC+AC)\}\\ &\quad +(E_x^2+E_z^2)\{\tfrac{1}{15}(A^2+B^2+C^2-AB-BC-AC)\}. \quad (23)\end{aligned}$$

Special Case No. 1.—Let plane polarized light ($E_z = E$, $E_y=0$, $E_x=0$) be incident in the direction OY and the observation be confined to the transverse direction OX. The molecule is characterized by $A \neq B \neq C$. Substituting in (21) and (23), we have

$$\overline{p_z^2} = E^2\{\tfrac{1}{5}(A^2+B^2+C^2)+\tfrac{2}{15}(AB+BC+AC)\}$$

$$\overline{p_y^2} = E^2\{\tfrac{1}{15}(A^2+B^2+C^2-AB-BC-AC)\}.$$

If the depolarization of the scattered light is denoted by ρ_v, we have

$$\rho_v = \frac{\overline{p_y^2}}{\overline{p_z^2}} = \frac{A^2+B^2+C^2-AB-BC-AC}{3(A^2+B^2+C^2)+2(AB+BC+AC)}. \quad .. \quad (24)$$

If we further denote $\tfrac{1}{3}(A+B+C)$, the mean polarizability of the molecule, by α and introduce a new parameter γ^2 in the place of $A^2+B^2+C^2-AB-BC-AC$, ρ_v may be alternatively written, after a slight readjustment, as follows :

$$\rho_v = \frac{\tfrac{3}{45}\gamma^2}{\alpha^2+\tfrac{4}{45}\gamma^2}. \quad .. \quad .. \quad .. \quad (24a)$$

Special Case No. 2.—Let us consider the case in which the polarizability ellipsoid of the molecule is a spheroid ($A=B\neq C$), other conditions remaining the same as in No. 1. We have

$$\overline{p_z^2} = \frac{E^2}{15}\{8A^2+3C^2+4AC\}$$

$$\overline{p_y^2} = \frac{E^2}{15}(C-A)^2$$

$$\rho_v = \frac{(C-A)^2}{8A^2+3C^2+4AC}.$$

This result is identical with that already deduced (see equation 18). Here again, the mean polarizability α will be represented by $\tfrac{1}{3}(2A+C)$ and the parameter γ^2 will reduce to $(C-A)^2$ and we may write ρ_v in the alternative notation as

$$\rho_v = \frac{\tfrac{3}{45}\gamma^2}{\alpha^2+\tfrac{4}{45}\gamma^2}.$$

Special Case No. 3.—Let unpolarized light ($E_z=E$, $E_y=0$, $E_x=E$) be incident in the direction OY and the observations confined to the transverse direction OX. The molecule is characterized by $A\neq B\neq C$. The depolarization ρ will be given by

$$\rho = \frac{2(A^2+B^2+C^2-AB-BC-AC)}{4(A^2+B^2+C^2)+AB+BC+AC}. \quad .. \quad (25)$$

In the alternative notation, this may be written as

$$\varrho = \frac{\frac{6}{45}\gamma^2}{\alpha^2 + \frac{7}{45}\gamma^2}. \qquad \text{(25a)}$$

Special Case No. 4.—Let us now consider the case in which the polarizability ellipsoid of the molecule is a spheroid ($A = B \neq C$), other conditions remaining the same as in No. 3. We have

$$\varrho = \frac{2\,(C-A)^2}{9A^2 + 4C^2 + 2AC}.$$

This result is identical with that already deduced (see equation 19). In the alternative notation, this reduces to (25*a*). It may be noted that when the molecules are optically spherically symmetrical ($A = B = C$), the depolarization reduces to zero in all the above cases, as it ought to. All these special cases could also have been deduced, each separately, by methods less elaborate than that employed for the general case.

✓ *Intensity of Light Scattered by Anisotropic Molecules.*—It has been shown (equation 5) that for spherically symmetrical molecules, the scattering power is proportional to α^2. If I_1 and I_2 are the intensities of scattering by two different gases, both at N.T.P., it is obvious that

$$\frac{I_1}{I_2} = \frac{\alpha_1^2}{\alpha_2^2} = \frac{(n_1-1)^2}{(n_2-1)^2}, \qquad \text{(26)}$$

where n_1 and n_2 are the refractive indices of the two gases respectively. This follows from the fact that $\alpha = \frac{n^2-1}{4\pi\nu}$ and n is nearly unity. This equation has to be slightly modified in the case of a gas consisting of anisotropic molecules. (25*a*) tells us that in such a case, the total intensity of the scattered beam, when unpolarized incident light is used, is enhanced by a term equal to $\frac{13}{45}\gamma^2$ for every α^2. It may easily be seen from (25*a*) that the following relationship exists between α, γ and ϱ.

$$\frac{13}{45}\gamma^2 = \frac{13\varrho\alpha^2}{6-7\varrho}. \qquad \text{(27)}$$

Adding $\frac{13}{45}\gamma^2$ for every α^2 and using (27), we may rewrite (26) as follows:

$$\frac{I_1}{I_2} = \frac{(n_1-1)^2\left(\dfrac{1+\varrho_1}{6-7\varrho_1}\right)}{(n_2-1)^2\left(\dfrac{1+\varrho_2}{6-7\varrho_2}\right)}. \quad \cdots \quad \cdots \quad (28)$$

It has already been shown that when unpolarized incident light is used, the intensity of the light scattered in a transverse direction, when expressed as a fraction of the total intensity of the incident light, is $\frac{8\pi^4}{\lambda^4}\cdot\frac{\alpha^2}{r^2}$ (see equation 6) for isotropic molecules. Enhancing this by an amount equal to $\frac{13}{45}\gamma^2$ for every α^2, we have the following equation for I, the intensity of the light scattered, per unit volume of a gas consisting of ν anisotropic molecules, in the transverse direction when expressed as a fraction of the total energy I_0 in the incident unpolarized light.

$$\frac{I}{I_0} = \frac{8\pi^4\nu}{r^2\lambda^4}\left\{\alpha^2 + \frac{13\varrho}{6-7\varrho}\alpha^2\right\} = \frac{8\pi^4\nu\alpha^2}{r^2\lambda^4}\left(\frac{6+6\varrho}{6-7\varrho}\right). \quad \cdots \quad (29)$$

CHAPTER IV

EXPERIMENTAL RESULTS IN GASES AND COMPARISON WITH THEORY

Introduction.—With the phenomenal development, in the hands of Lord Rayleigh, of the theory of light scattering by molecules, the conviction that the sky light and its imperfection of polarization are only consequences of molecular scattering grew stronger and the great importance of carrying out experiments on the subject of light scattering in gases in the laboratory was soon realized. On account of the extreme feebleness of the scattered light, numerous difficulties confronted the investigators. Cabannes[1], for the first time, observed the genuine scattering by dust-free air in the year 1915. Three years later, Lord Rayleigh[2] made systematic investigations on the subject and worked with several other gases besides air. A large amount of literature relating to the measurements of depolarization and intensity of the light scattered by gases has appeared subsequent to these pioneering investigations. Many important questions that have arisen from time to time relating to the experimental technique have also been discussed at length. From the point of view of the present section, the subject may be divided into two portions, namely, work done prior to the discovery of the Raman effect and work done subsequent to it. Amongst the earlier investigators, the names of Cabannes, Rayleigh, Wood, Smoluchowski, Gans, Raman and collaborators may be mentioned. During the latter period, the main workers were Parthasarathy, Ananthakrishnan and Volkmann. Although the various investigators cited above had much in common from an experimental point of view, it may be remarked here that the more recent authors had to bear in mind the fact that the entire subject of the depolarization of scattered light took a new and important turn since the

[1] Comptes Rendus, *160*, 62 (1915).

[2] Proc. Roy. Soc., *94*, 453 (1918).

discovery of the Raman effect. As a result of this increased significance, the experimental technique has greatly been improved and the main issues involved therein considerably clarified by these authors.

A Brief Description of the Experimental Arrangements.—Before we discuss the experimental details and their significance, we may briefly describe here the arrangements originally employed by Cabannes and by Lord Rayleigh. Fig. 6 represents the apparatus used by Cabannes. S is a quartz

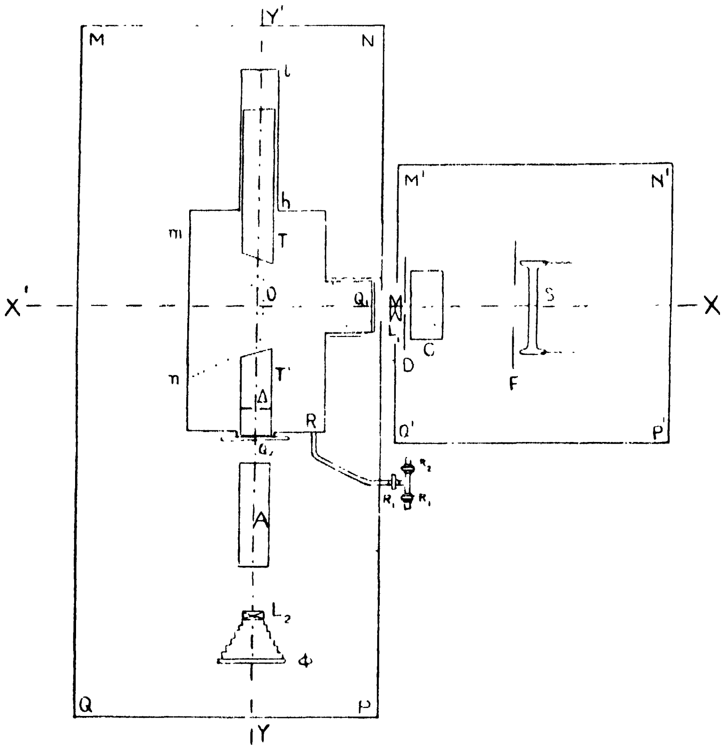


FIG. 6.

mercury lamp situated at a distance of 20 cms. from a condensing lens L_1 which is made up of a pair of plano-convex quartz lenses, the combination having a focal length of 10 cms. R is

the container for the gas. F and D are apertures. Q_1 and Q_2 are quartz windows which permit the passage of incident and scattered beams respectively. L_2 is a large aperture quartz lens used for the purpose of photographing the scattered beam. A double image prism is placed in the path of the scattered beam between Q_2 and L_2 so as to separate the vertical and horizontal components. The apparatus and the illuminating arrangements are each enclosed in separate boxes so as to prevent fogging of the photographic plate by the action of direct light.

The arrangements in Lord Rayleigh's experiments are essentially similar and are shown in Fig. 7. The container is a

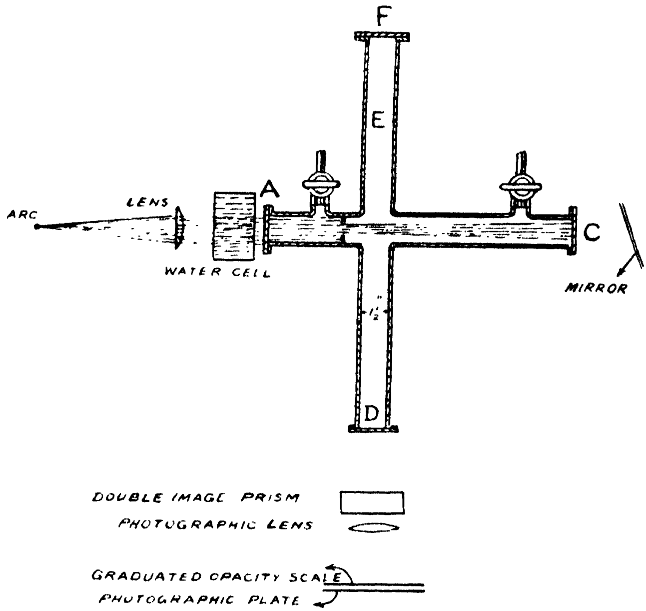


FIG. 7.

cross of brass tubing having an internal diameter of 1½ inches. The inside is blackened. The beam is incident along AC and the scattered light is observed through D. Before it is photographed, it passes through a double image prism which separates the vertical component in the beam from the horizontal one. The tube E, whose end is closed with a blackened brass disc

F, affords a black background against which the track is viewed or photographed. Diaphragms are inserted at suitable places. A carbon arc taking a current of about 25 amperes and giving a large intensity is used as the illuminating source. The radiation from the positive crater of the arc is rendered parallel by means of a plano-convex lens of 4 inches focal length.

From the descriptions given above, it will be noticed that amongst the features which are of importance to an experimenter in this subject are: (i) source of radiation, (ii) method of illumination, (iii) container for the gas, (iv) suitable background and elimination of parasitic light, and (v) method of observation. These points will be dealt with and discussed individually in the following pages.

Source of Radiation.—All sources of radiation used so far by different investigators fall into two classes, namely, sun-light and artificial sources. The intensity of sun-light when concentrated with a large aperture lens exceeds considerably that of any artificial source and thus there is a distinct advantage in using sun-light when working with weakly scattering substances such as gases. On the other hand, the fact that it is not available in all seasons and at all times of the day and the fact that it is often of a very fluctuating character render it somewhat unsuitable for this type of work. Nevertheless, it has been employed by Cabannes in his later investigations and very extensively by Raman and his collaborators in India.

Amongst the artificial sources, mention may be made of the mercury arc and the carbon arc. It has already been mentioned that a mercury arc was used by Cabannes (Fig. 6) in his earliest investigations, whereas Lord Rayleigh used a carbon arc (Fig. 7). Amongst other useful sources are the pointolites of various types. While these artificial sources possess the advantage of having a more or less constant intensity and of being capable of service at all times, they are never of such a large intensity as concentrated sun-light.

Method of Illumination with Special Reference to Convergence Correction.—As has been mentioned in the foregoing paragraph, it is practically impossible to get a beam of light of sufficient intensity for purposes of light scattering work without

using a condensing lens of some kind. All formulae derived hitherto apply only to directions which are strictly transverse to the direction of propagation of the incident beam. In order that a satisfactory and rigorous comparison between experiment and theory may be possible, observations must be confined to transversely scattered rays only. This is possible in practice, only if we use a parallel beam of light for purposes of illumination; but a parallel beam of any kind, artificial or natural, cannot be obtained with the requisite intensity particularly when we are working with gases. Usage of a condensing lens on the other hand, while furnishing increased intensity at the focus, involves convergent rays. Observations at the focus, even when confined to a lateral direction with respect to the axis of the lens, include rays scattered in a direction other than transverse and thus the observed results are no longer comparable with the conclusions of the theory. The error will naturally depend on the extent of convergence, which in its turn will depend on the aperture of the condensing lens. It is thus seen that a condensing lens of a large aperture, while being an advantage from the view-point of intensity, is a distinct disadvantage from the view-point of convergence errors. In this respect, we must also bear in mind that there is an important difference between sources such as sun-light, carbon arc, pointolites, etc., on the one hand, and the mercury arc on the other. In the first type of sources, the rays are all symmetrically disposed around the axis of the lens, whereas in the latter they are not so disposed. The finite size of the source and the image cause an additional complication and the problem of convergence correction becomes more difficult of solution.

The whole question of convergence correction is of utmost importance, particularly when we are dealing with depolarization factors which are relatively small such as are met with in gases. Cabannes,[1] Ramanathan and Sreenivasan,[2] Gans,[3] Ramakrishna

[1] Ann. d. Physique, *15*, 113 (1921).
[2] Phil. Mag., *1*, 493 (1926).
[3] Physikal Z., *28*, 661 (1927).

Rao[1] and Ananthakrishnan[2] are amongst those who have tackled this problem but there has been a considerable amount of divergence of opinion regarding the magnitude of the error arising on this score. There has been no agreement even on the important and fundamental question as to the existence or otherwise of any error due to convergence, not to talk of its magnitude.

For instance, Ramakrishna Rao concluded that if observations are made precisely at the focus of a condensing lens, it is unnecessary to correct for convergence errors. On the other hand, Gans was of the opinion that there is a finite and appreciable correction to be applied amounting to $\frac{\Omega^2}{2}$, where Ω is the semi-angle of convergence. The view-points of these two investigators are entirely different. The former assumed that the individual rays meeting at the focus of a lens are optically coherent whereas the latter assumed that they are incoherent. Ramakrishna Rao made some experimental observations on the depolarization of scattered light in pentane and carbon tetrachloride, condensing the incident light with a lens of 3 inches diameter and 12 inches focal length. He obtained the same values of depolarization with apertures of the lens equal to 3 inches, 2 inches and 1 inch respectively giving semi-angles of convergence 7°, 4·6°, 2·3°, thus supporting his contentions that the depolarization factor, when observations are made at the focus, is independent of the extent of convergence. On the other hand, observations made by Cabannes[3] with varying angles of convergence showed that the depolarization is subject to a definite correction on the score of convergence when condensing lenses are used. His results did not, however, quantitatively support the expression derived by Gans but showed that the convergence correction was somewhat smaller, being of the order of $\frac{\Omega^2}{4}$.

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[1] Ind. Jour. Phys., *2*, 61 (1927).

[2] Proc. Ind. Acad. Sci., *2*, 133 (1935).

[3] La Diffusion Moleculaire de La Lumiere (1929).

Ananthakrishnan has also recently carried out extensive experimental investigations, choosing isobutane gas as a standard, because it exhibits a low depolarization value and at the same time possesses a large scattering power. The results obtained by him with a high class condensing lens in combination with an adjustable iris diaphragm are given below in Table I.

TABLE I

Convergence Correction

Convergence of the incident beam 2Ω		Observed depolarization ρ'	Correction $\frac{\Omega^2}{2}$	Corrected value of depolarization ρ
Degrees	Radians			
29°48′	0·520	4·04%	3·38%	0·66%
19°48′	0·346	2·27%	1·45%	0·82%
9°54′	0·173	1·06%	0·37%	0·69%

The fact, that the value of ϱ' as observed varies considerably with varying apertures, shows that there is an unmistakable convergence error. The fact, that the value of ϱ obtained after correcting for the term $\frac{\Omega^2}{2}$ remains more or less constant, shows that the correction applied is of the right order of magnitude.

From the point of view of theory, both Gans and Ananthakrishnan have considered this problem in some detail. Gans assumes that the rays coming from different portions of a converging lens are incoherent when they are brought to a focus and his treatment of the problem is given in Appendix II. He arrives at the result that a correction amounting to $\frac{\Omega^2}{2}$, where Ω is the semi-angle of convergence, has to be applied in every case. Unlike Gans, Ananthakrishnan makes the assumption that the rays starting from a given point on the source are to be regarded as coherent when they are brought to a focus at the conjugate point by a condensing lens. In such a case, it may be shown that the contentions of Ramakrishna Rao are correct,

provided we are able to observe the scattering only at the interference maxima. At the interference minima, the resultant vector is, however, turned round and is no longer parallel to the original vibration vector and the state of polarization of the scattered light is therefore reversed. In practice, owing to various complications such as the excessive closeness of the interference bands, it is not possible to isolate the scattered light emanating from the region of interference maxima alone from the rest. Accordingly the effect observed in the usual way is that averaged over the whole field. We shall not go into the details of Ananthakrishnan's treatment but only point out that, when such an averaging is performed in theory, having due regard to the distribution of intensity in the field, exactly the same results are obtained as have been obtained by Gans on the assumption that the rays are altogether incoherent.

It has also been noticed by Ananthakrishnan, that as a condition for the validity of the above treatment, it is necessary that every part of the lens is equally effective at any given point in the focal plane where there is any appreciable intensity. Such a condition is satisfied to a reasonable extent only by high class lenses and it is therefore necessary that a really good quality lens be used in experiments on light scattering so that the convergence error may be calculated and corrected for definitely. It thus appears that both experimental and theoretical evidences are now overwhelmingly in favour of applying a correction on the score of convergence. We may conclude that the best method of illumination is to condense sun-light or light from a brilliant point source (preferably sun-light) with a good quality lens and confine the observations to the focal plane. Values of depolarization so obtained should be subjected to a correction to the extent of $\frac{\Omega^2}{2}$ where Ω is the semi-angle of convergence.

Container for Gas.—The containers that are suitable for these investigations may broadly be divided into two classes, namely, crosses and bulbs. Both metallic and glass crosses have been constructed and also bulbs of different shapes have been tried from time to time. A typical example of a metallic

cross has already been described when dealing with the earlier work of Lord Rayleigh. Raman and collaborators have used metallic crosses of different types. A noteworthy modification of the principle of the cross has been introduced by Raman and Ramanathan[1] for the study of the scattering of light in compressed gases. They constructed a container of the shape shown in Fig. 8, consisting of a massive solid steel cylinder 20 cm. long and 6·5 cm. in diameter, in which two holes at right angles to each other were bored. The ends A and B, which served as the illumination and observation windows respectively, were sealed with conically ground glasses. A pin valve was fitted to the end D and the opening at C was closed up. To secure a good background, a plate of black glass M was fitted at an angle of 45° inside the cylinder. Gases at pressures up to 100 atmospheres could be held in this container. Raman and Ramanathan studied the scattering of light in carbon dioxide for the first time at such pressures.

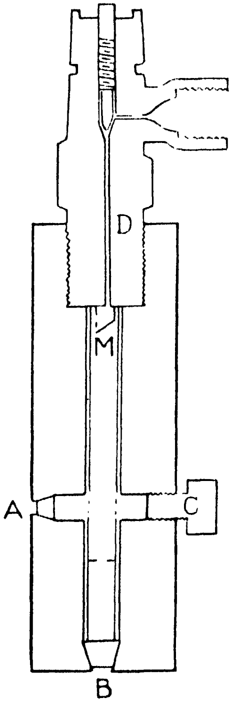


FIG. 8.

Improved forms of metallic crosses, suitable for the study of the depolarization and the intensity of light scattering in gases at high pressures, have subsequently been devised by Bhagavantam[2] and by Weiler.[3] Bhagavantam's apparatus is shown diagrammatically in Fig. 9. Four strong steel tubes are screwed on to a rectangular steel chamber in which two holes are drilled at right angles to each other. They serve to connect the two pairs of opposite tubes, making the apparatus resemble a hollow

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[1] Proc. Roy. Soc., *104*, 357 (1923).
[2] Ind. Jour. Phys., *7*, 107 (1932).
[3] Ann. d. Phys., *23*, 493 (1935).

cross. Light enters through steel tube 1 and passes off into the opposite tube without striking any of the walls and is absorbed

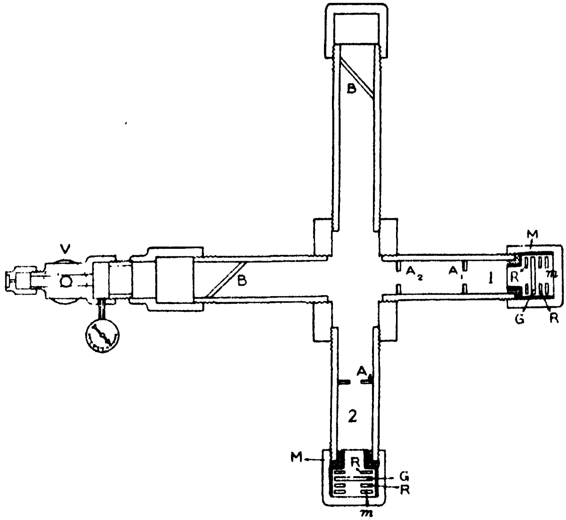


FIG. 9.

by a suitably placed black glass at the other end. The scattered light emerges out through the tube 2 and is taken into the spectrograph. Opposite the observation tube is another inclined black glass B so that any light that may get to the back by reflection at the walls is partly absorbed and partly reflected away from the slit of the spectrograph. Tubes 1 and 2 are provided with glass windows, $\frac{3}{8}$ inch thick, for the entry and the exit of the light. These are held between thick rubber washers to prevent leakage of gas. In the figure, the glass window is indicated by G, rubber washers by R and an iron washer by *m*. All these are contained in a metallic ring M, the purpose of which is partly to prevent spreading out of the rubber when squeezed. They are screwed on to the steel tube by a nut of suitable size. Two apertures A_1 and A_2 in the tube through which the incident light passes and one, A_3, in the observation tube serve the very useful purpose of preventing the light from falling directly on the walls of the steel chamber and giving rise

to parasitic light. The gas is admitted through a pin valve V after evacuating the whole apparatus and the pressure is read on a gauge attached to the pin valve. Pressures up to 75 atmospheres can be used in this apparatus.

Weiler's apparatus is shown in Fig. 10. A steel block M (100×100×120 mm.) is bored through at right angles and transparent glass windows are provided at three holes B, E and E. The latter two serve for illumination and B is for observation. The glass windows are 15 mm. thick and have a diameter of 40 mm. V represents the volume of gas which scatters the light and is about 20 c.c. A closed tube H of 20 cm. length provides the necessary background. The pressures are read through a gauge reading to 0·2 atmospheres and the temperatures through a thermometer reading to 0·2°C., both fitted into the cross. Pressures up to 80 atmospheres have been reached with this apparatus.

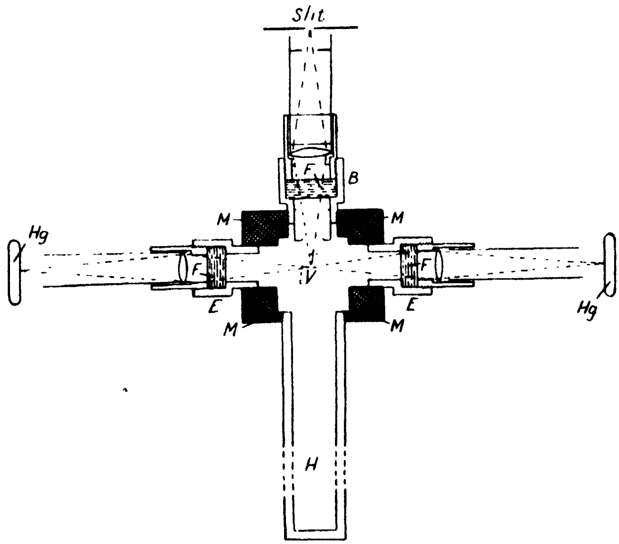


FIG. 10.

Cabannes constructed the first glass cross (Fig. 11) which is made up of two identical tubes, each having an internal

diameter of 3 cms., the total capacity of the cross being 300 c.c. The investigations could thus be extended also to vapours which are either not available in large quantities or which cannot be used in metallic containers on account of their chemical action on the metal, paints, etc. Ramanathan and Sreenivasan [1] used glass bulbs of special shape (Fig. 12) into which light was admitted from the side at A and the scattered beam examined through the front portion at B. Ramakrishna Rao [2] modified the form of the central portion of the bulb and showed that it was

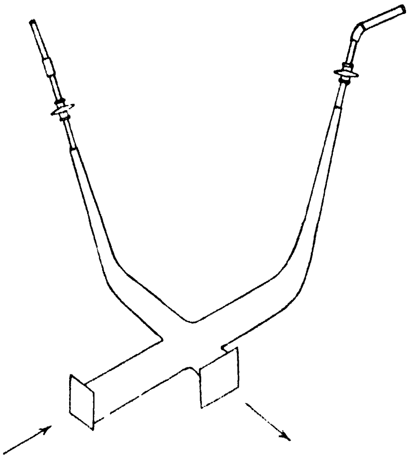


FIG. 11.

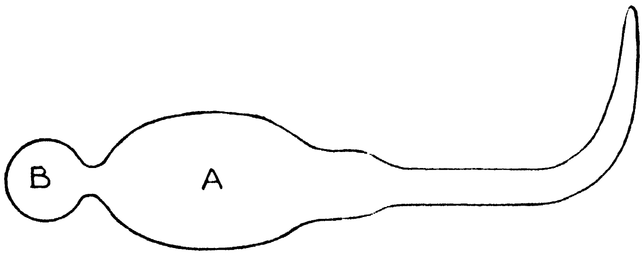


FIG. 12.

an advantage to have it ellipsoidal instead of spherical as in the former case, light reflected from the sides is avoided more effectively than in the latter. Amongst the more recent investigators, Parthasarathy [3] and Volkmann [4] used metallic

[1] Proc. Ind. Assoc. Cult. Sci., *9*, 203 (1926).
[2] Ind. Jour. Phys., *2*, 61 (1927).
[3] *Ibid.*, *7*, 139 (1932).
[4] Ann. d. Phys., *24*, 457 (1935).

crosses similar to the older types, whereas Ananthakrishnan [1] constructed glass crosses of a much larger size and improved pattern. Ananthakrishnan closely examined the relative merits of the two types of containers and came to the conclusion that a glass cross with suitable apertures and flat windows was to be definitely preferred to a bulb of any shape for accurate depolarization work.

Suitable Background and Elimination of Parasitic Light.— It is of utmost importance to avoid scrupulously light being reflected directly into the observer's eye, as even a very small fraction of it would considerably vitiate the results regarding the depolarization measurements. The following precautions have to be taken for this purpose. In all metallic containers, suitable apertures must be provided (Figs. 7 and 9), a dull black glass whose plane is inclined at 45° to the direction of observation must be included in the arm opposite the observation window so as to furnish a dark background (see M in Fig. 8) and this arm must be made as long as possible consistent with the other dimensions. The inside of the cross may be painted black if the chemical nature of the gas under investigation permits it. In all glass containers, suitable blackened apertures should be provided at the proper places and the apparatus painted black on the outside. The arm opposite the observation window should be drawn out into the shape of a horn so that any radiation reaching this end may be totally absorbed within the horn by repeated reflections. In the case of bulbs, special care must be taken to paint all the outside of the bulb black, leaving only three windows, one for illumination, one for exit of the illuminating beam and another for observation.

Method of Observation.—For the measurement of the depolarization of the scattered light, two distinct methods, namely, the photographic and the visual, may be employed. In the original investigation of Lord Rayleigh, which is typical of the photographic method, a double image prism in the path of the scattered beam separated the horizontal and the vertical components from each other. The two beams thus separated fell on a

[1] Proc. Ind. Acad. Sci., *2*, 153 (1935).

photographic plate in front of which was another glass plate on which an opacity scale had been formed earlier (see Fig. 7). The stronger or the vertical component had to pass through the less transparent portions, while the horizontal or the weaker component was made to pass through the more transparent portions of the front glass. A series of exposures was made, moving the opacity scale along, and the particular opacity which approximately equalized the intensities was easily decided upon after development. In this way the ratio of the horizontal to the vertical component was determined for a series of gases.

Cabannes also measured the depolarization factors by the photographic method. He replaced the opacity scale by a nicol which could be rotated on a graduated circle. The two components of the scattered beam passed through the nicol and the nicol was rotated by trial to such a position that the two images were recorded with equal brightness. If V and H represent the intensities of the two components which are to be compared, it is easily seen that there will be four positions of the nicol in which the two components will appear equally bright. If 2θ represents the angle between two such positions, situated symmetrically with respect to the horizontal vibration direction, we have

$$V \sin^2\theta = H \cos^2\theta \quad \text{or} \quad \varrho = \frac{H}{V} = \tan^2\theta.$$

Instead of photographing the two images, one can easily make a visual examination and find the required positions. Several readings of 2θ are usually obtained and the average value taken. In the more recent investigations, the visual method has practically replaced the more elaborate photographic method. The images must be clearly separated without any trace of overlapping and viewed against a perfectly dark background. For obtaining the best results, they should be neither too intense nor too faint.

In the matter of measuring the intensity of the scattered light also, both photographic and visual methods may be employed. In the visual method, first used by Lord Rayleigh, the scattered light was viewed through a telescope and a white surface inclined at 45° was placed in its focal plane and arranged

so as to cover half the field. This white surface was illuminated by a beam derived from another white surface exposed to the same arc as was used to illuminate the gas. The colour of the direct light was made to match with that of the scattered light by inserting a pale cobalt glass in the path of the comparison beam and its intensity was made to match by inserting a photometric wedge. Any fluctuations in the intensity of the illuminating arc did not matter as the scattered beam and the comparison beam were both affected equally. Different gases were compared with air by suitably adjusting the pressures so as to give the same wedge reading. Assuming proportionality between the intensity of scattering and the pressure of a gas, the relative scattering powers of different gases were easily estimated.

Lord Rayleigh developed a photographic method also. In this method, the scattered beam in the gas possessing the lesser scattering power was first photographed with the lens at full aperture. The scattered beam in the other gas under comparison was then photographed on the same plate in a series of exposures, by keeping the time of exposure constant but varying the aperture of the lens. The diminution of aperture, necessary for reducing the intensity of scattering in one gas to match with that of the other, was obtained from the photographs with the help of a photometer. The ratio of the scattering powers is then deduced by comparing the areas of the apertures used. The success of the method obviously depends upon the constancy of the intensity of the source. Lord Rayleigh used a quartz mercury arc which was run long enough before beginning the exposures to have attained a steady state. Methods employed subsequently by other investigators are not essentially different.

Details of a Complete Apparatus.—After having discussed the various points involved in fixing up a suitable experimental technique for examining the scattered light in gases, we shall now describe the details of an apparatus recently used by Ananthakrishnan. This combines in it the advantages of all the older methods and has been evolved with due regard to all the important issues raised in the foregoing pages. The essential features are given in italics. The apparatus (Fig. 13) consists of a *cross made of pyrex glass of about a litre in capacity.* The

glass tube employed has an internal diameter of 4 cms. and three of the arms are each 20 cms. long. The fourth arm, which is opposite the observation side, is longer and is *drawn out and bent into the shape of a horn.* To the end of the horn is attached a pyrex stop-cock for the admission of gas into the cross. Suitable *diaphragms of oxidized brass* are put at proper places inside the cross so as to ensure the most complete elimination of parasitic light. The apertures in the diaphragms have a diameter of about ½ inch. The surfaces of the diaphragms are rendered black by immersing them in an ammoniacal solution of copper carbonate. The open ends of the three arms are closed by fusing *specially chosen, strain free, flat, pyrex glass plates.* The outside of the whole cross, excepting the end windows, is

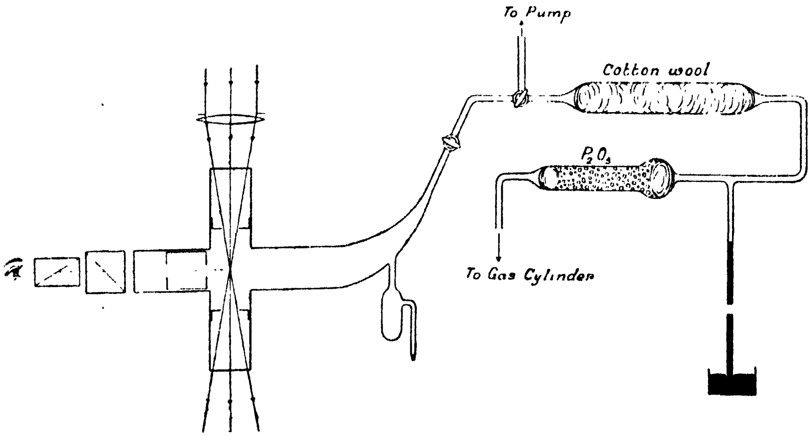


FIG. 13.

painted dull black. Observations are made inside a dark cabin. Sun-light is used for illumination. *A Dallmeyer photographic lens of adjustable aperture,* and focal length 12 inches, serves to concentrate the sun-light at the centre of the cross. The gases are admitted into the cross through a tube of *anhydrous phosphorus pentoxide* and a *long plug of compressed cotton wool* after *evacuating the whole system. Rubber connections are avoided as far as possible.* Depolarization measurements are made *visually by the Cornu method. A correction for convergence*

amounting to $\frac{\Omega^2}{2}$, where Ω is the semi-angle of convergence, *is always made.*

Depolarization Factors and Optical Anisotropy.—Cabannes has given an excellent summary of all the experimental results that have been obtained prior to 1929. In Table II, we shall give the values adopted by Cabannes in his book along with the more recent determinations of Parthasarathy, Ananthakrishnan and Volkmann. A new parameter δ, which has to be regarded as a measure of the optical anisotropy, may be introduced at this stage, as it will be of use in the succeeding chapters. The significance of the new parameter and the relation which it bears to those already introduced are given in equations 1, 1*a* and 2. 1*a* relates to the case where $A = B \neq C$ and may be obtained from 1 by putting $B = A$ in it. In either case $\delta = \gamma^2/9\alpha^2$. Since ϱ is given by (25) of chapter III, relations (2) easily follow. All the figures given in Table II relate to unpolarized incident light and refer only to the gaseous or vapour states. δ calculated with the help of (2) from the observed values of ϱ is also given in the Table for each one of the molecules.

$$\delta = \frac{A^2+B^2+C^2-AB-BC-AC}{(A+B+C)^2} \quad \ldots \quad \ldots \quad (1)$$

$$\delta = \frac{(A-C)^2}{(2A+C)^2} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (1a)$$

$$\varrho = \frac{6\delta}{5+7\delta} \text{ and } \delta = \frac{5\varrho}{6-7\varrho}. \quad \ldots \quad \ldots \quad (2)$$

It may be noted that the most probable values of ϱ for two important cases, namely argon and methane, have been given as zero. This conclusion is based on the recent work of Ananthakrishnan and Volkmann. In the case of argon, although Ananthakrishnan gave the value as 0·42, he expressed the opinion that in all probability it was due to impurities. In the case of methane, Ananthakrishnan's value is quite small, much smaller than any given hitherto, whereas Volkmann actually gives it as zero. This removes a long standing difficulty in respect of the origin of the optical asymmetry in an apparently

TABLE II *

Depolarization of Light Scattered by Gases and Vapours : 100ρ

Section i

Substance	Formula	Value adopted by Cabannes	Parthasarathy	Ananthakrishnan	Volkmann	Best representative or most probable value	$\delta \times 10^3$	C/A
Atoms :								
Argon	A	0·5	0·56	0·42	..	0	0	1
Diatomic homopolar molecules :								
Hydrogen	H_2	2·7	2·57	..	0·9	?	..	..
Nitrogen	N_2	3·6	3·55	..	..	3·6	31·3	1·64
Oxygen	O_2	6·4	6·50	..	..	6·5	58·6	1·95
Chlorine	Cl_2	4·3	4·07	..	..	4·1	35·9	1·70
Air	..	4·15	4·15	..	..	4·2	36·8	..
Diatomic heteropolar molecules :								
Nitric oxide	NO	2·6	2·68	..	..	2·7	23·2	1·54
Carbon monoxide ..	CO	2·1	1·30	..	..	1·3	11·0	1·35
Hydrogen chloride ..	HCl	0·7	0·71	..	..	0·7	5·9	1·25
,, bromide ..	HBr	..	0·84	..	..	0·8	6·7	1·27
,, iodide ..	HI	..	1·27	..	..	1·3	11·0	1·35
Triatomic molecules :								
Carbon dioxide ..	CO_2	9·8	9·72	..	7·24	9·7	91·1	2·30
,, disulphide ..	CS_2	11·5	..	..	..	11·5	110·7	2·50
Nitrous oxide ..	N_2O	12·5	12·47	12·95	10·2	12·5	122·0	2·61
Carbonyl sulphide ..	COS	..	8·77	..	..	8·8	81·7	2·19
Water *	H_2O	2·0	..	..	..	2·0	17·1	..
Hydrogen sulphide ..	H_2S	1·0	0·93	0·30	..	0·3	2·5	..
Sulphur dioxide ..	SO_2	4·5	3·11	..	..	3·1	26·8	..
Simple hydrocarbons :								
Methane	CH_4	1·5	1·12	0·34	0	0	0	1
Ethane	C_2H_6	1·6	1·30	0·50	..	0·5	4·2	1·21
Propane	C_3H_8	1·6	1·51	0·66	..	0·7	5·9	1·25
Butane	C_4H_{10}	1·7	1·51	0·85	..	0·9	7·6	1·28
Isobutane	C_4H_{10}	..	1·03	0·46	..	0·5	4·2	..
Pentane	C_5H_{12}	1·3	..	..	..	1·3	11·0	1·35
Isopentane	C_5H_{12}	1·3	..	..	..	1·3	11·0	..
Hexane	C_6H_{14}	1·5	..	..	..	1·5	12·7	1·38
Heptane	C_7H_{16}	1·6	..	..	..	1·6	13·6	1·40
Octane	C_8H_{18}	1·8	..	..	..	1·8	15·3	1·42
Ethylene	C_2H_4	..	2·92	..	..	2·9	25·0	1·56
Acetylene	C_2H_2	..	4·52	..	..	4·5	39·6	1·75
Cyclopropane ..	C_3H_6	..	..	0·52	..	0·5	4·2	0·82
Propylene	C_3H_6	..	..	2·91	..	2·9	25·0	..
Other simple molecules :								
Ammonia	NH_3	1·3	0·98	..	..	1·0	8·4	0·75
Carbon tetrachloride ..	CCl_4	0·52	0·62	0·15	..	0·2	1·7	..
Silicon tetrachloride ..	$SiCl_4$	..	1·64	..	..	1·6	13·6	..
,, tetrafluoride ..	SiF_4	..	3·11	..	..	3·1	26·8	..
Methyl chloride ..	CH_3Cl	1·5	2·04	1·95	..	2·0	17·1	0·65
Methylene chloride ..	CH_2Cl_2	..	2·93	..	..	2·9	25·0	..
Chloroform	$CHCl_3$	1·8	1·78	..	..	1·8	15·3	0·67
Ethyl chloride ..	C_2H_5Cl	1·6	..	1·49	..	1·5	12·7	..
Methyl ether	C_2H_6O	..	1·56	1·20	..	1·2	10·1	..
Ethyl ether *	$C_4H_{10}O$	2·7	2·51	..	..	2·5	21·5	..
Acetone *	C_3H_6O	1·8	1·62	..	..	1·6	13·6	..
Allyl alcohol *	C_3H_6O	2·8	2·40	..	..	2·4	20·6	..
Formaldehyde ..	CH_2O	..	1·88	..	..	1·9	16·2	..
Acetaldehyde ..	C_2H_4O	..	2·68	..	..	2·7	23·2	..
Methylamine	CH_5N	..	0·77	..	..	0·8	6·7	..
Ethylamine	C_2H_7N	..	0·97	..	..	1·0	8·4	..

Section ii

Substance	Formula	100ρ	$\delta \times 10^3$	Substance	Formula	100ρ	$\delta \times 10^3$
Benzene	C_6H_6	4·5	39·6	Ethyl formate ..	$C_3H_6O_2$	2·2	18·8
Toluene	C_7H_8	4·3	37·7	Propyl ,, ..	$C_4H_8O_2$	1·8	15·3
Meta-xylene ..	C_8H_{10}	5·0	44·2	Formic acid ..	HCOOH	4·1	35·9
Ethyl benzene ..	C_8H_{10}	4·7	41·4	Acetic ,, ..	$C_2H_4O_2$	3·0	25·9
Cyclohexane ..	C_6H_{12}	1·0	8·4	Propionic ,, ..	$C_3H_6O_2$	2·7	23·2
Cyclohexene ..	C_6H_{10}	2·2	18·8	Butyric ,, ..	$C_4H_8O_2$	2·0	17·1
Methyl cyclohexene ..	C_7H_{12}	2·2	18·8	Acetic anhydride ..	$C_4H_6O_3$	1·9	16·2
β Isoamylene ..	C_5H_{10}	2·4	20·6	Propionic ,, ..	$C_6H_{10}O_3$	2·9	25·0
Naphthalene ..	$C_{10}H_8$	7·9	72·5	Methyl ethyl ketone ..	C_4H_8O	2·2	18·8
Ethylene chloride ..	$C_2H_4Cl_2$	3·4	29·5	Methyl propyl ,, ..	$C_5H_{10}O$	2·0	17·1
Propyl chloride ..	C_3H_7Cl	1·5	12·7	Diethyl ketone ..	$C_5H_{10}O$	3·2	27·7
Isobutyl ,, ..	C_4H_9Cl	1·7	14·5	Methyl acetate ..	$C_3H_6O_2$	2·2	18·8
Ethyl bromide ..	C_2H_5Br	2·3	19·7	Ethyl acetate ..	$C_4H_8O_2$	2·2	18·8
Propyl ,, ..	C_3H_7Br	2·1	17·9	Propyl acetate ..	$C_5H_{10}O_2$	1·5	12·7
Isobutyl ,, ..	C_4H_9Br	1·6	13·6	Chlorobenzene ..	C_6H_5Cl	4·9	43·3
Ethylene ,, ..	$C_2H_4Br_2$	3·7	32·2	Bromobenzene ..	C_6H_5Br	5·3	47·1
Bromoform ..	$CHBr_3$	3·1	26·8	Nitrobenzene ..	$C_6H_5NO_2$	6·1	54·7
Isopropyl iodide ..	C_3H_7I	2·3	19·7	Aniline ..	$C_6H_5NH_2$	6·1	54·7
Methyl alcohol ..	CH_3OH	1·7	14·5	O. Nitrotoluene ..	$C_7H_7NO_2$	5·2	46·1
Ethyl ,, ..	C_2H_5OH	0·9	7·6	M. ,, ..	$C_7H_7NO_2$	5·6	49·9
Propyl ,, ..	C_3H_7OH	1·2	10·1	Benzyl chloride ..	C_7H_7Cl	4·7	41·4
Isopropyl ,, ..	C_3H_7OH	1·3	11·0	Benzal chloride ..	$C_7H_6Cl_2$	4·4	38·7
Butyl ,, ..	C_4H_9OH	1·7	14·5	Benzoic acid ..	$C_7H_6O_2$	5·7	50·9
Isobutyl alcohol ..	C_4H_9OH	0·8	6·7	Methyl benzoate ..	$C_8H_8O_2$	5·9	52·8
Amyl ,, ..	$C_5H_{11}OH$	1·3	11·0	Salicylic acid ..	$C_7H_6O_3$	5·7	50·9
Isoamyl ,, ..	$C_5H_{11}OH$	1·1	9·3	Pyridine ..	C_5H_5N	4·8	42·4
Trimethyl carbinol ..	$C_4H_{10}O$	0·7	5·9	Quinoline ..	C_9H_7N	7·9	72·5
Methyl formate ..	$C_2H_4O_2$	2·2	18·8				

* Section i comprises of simple molecules and such others which have been re-investigated subsequent to 1929 or investigated for the first time by Parthasarathy, Ananthakrishnan or Volkmann. Section ii comprises of molecules which have been investigated only prior to 1929. As such, the values given in this section are merely those adopted by Cabannes and refer mostly to the work either of Cabannes or of Ramakrishna Rao. With the exception of methyl ethyl ketone, methyl propyl ketone, diethyl ketone, methyl benzoate and quinoline, the values have all been corrected, either by Ramakrishna Rao or by Cabannes, for departures from Boyle's law on account of the fact that most of the vapours were studied just above their respective boiling points. The necessity for such a correction will be evident when we deal with dense media. Values given in column 3 of section i against the four substances marked with asterisk are those of Ramakrishna Rao and have been corrected by him in the above manner.

spherically symmetrical atom like argon or a molecule like methane.[1] The result is in perfect accordance with the failure

[1] Recently Breazeale [Phys. Rev., *49*, 625 (1936)] has reported that methane shows a measurable electro-optical Kerr effect. This result implies an optical anisotropy and is in conflict with Volkmann's results.

of Bhagavantam[1] and of Lewis[2] to obtain pure rotational Raman scattering in methane even on prolonged exposures. In view of this, it may be of interest to re-examine the two other tetrahedral molecules, namely silicon tetrachloride and tetrafluoride, for which Parthasarathy found fairly high depolarization factors. The case of carbon tetrachloride is also somewhat puzzling. In these cases, however, the presence of an appreciable proportion of unsymmetrical isotopic molecules may be responsible for at least part of the observed depolarization. It is disconcerting to note that the important and fundamental case of hydrogen has yet no definite value of ρ ascribed to it.

The relatively large optical anisotropies exhibited by the aromatic compounds when compared with the aliphatic ones, the relatively large optical anisotropies exhibited by the homopolar molecules when compared with the heteropolar ones and the increasing optical anisotropy in the series ethane, ethylene and acetylene are the other notable results.

Relative Intensities of the Scattered Light.—We have seen that according to the elementary theory of light scattering by spherically symmetrical molecules, the scattering power of a gas is proportional to $(n—1)^2$ where n is the refractive index of the gas. The earliest results obtained by Lord Rayleigh substantiated this conclusion in the main. The following Table is reproduced from his work.

TABLE III

Ratio of Intensities of Scattered Light

Gas	Method of observation	Intensity of Scattered light	$(n-1)^2$
Air	Assumed ..	1·00	1·00
Hydrogen ..	Visual	0·230	0·229
Nitrous oxide ..	Photographic ..	3·40	3·12
Ether vapour ..	Mean of visual and photographic.	26·8	27·1

[1] Nature, *130*, 740 (1932).

[2] Phys. Rev., *41*, 389 (1932).

Subsequent careful experiments of Cabannes have, however, shown that the law is only approximately correct, and that there are appreciable and important deviations in certain cases, as may be expected. It has already been said that in the case of molecules that are not spherically symmetrical, the law is to be modified and represented by (28) of chapter III. Cabannes [1] obtained experimental results in support of this more accurate equation and these are given below.

TABLE IV

Ratio of Intensities of Scattered Light

Gases	Observed ratio	$\frac{(n_1-1)^2}{(n_2-1)^2}$	$\frac{(n_1-1)^2 \left\{\frac{1+\rho_1}{6-7\rho_1}\right\}}{(n_2-1)^2 \left\{\frac{1+\rho_2}{6-7\rho_2}\right\}}$
Argon / Nitrogen ..	0·829	0·90	0·832
Carbon dioxide / Argon ..	3·31	2·53	3·13
Carbon dioxide / Air ..	2·62	2·35	2·65
Carbon dioxide / Oxygen ..	2·93	2·80	3·00
Hydrogen / Oxygen ..	0·255	0·276	....

The values given in column 4 are based on the revised values of ϱ given in Table II and are slightly different from those given by Cabannes. The distinctly better agreement between the observed values and those of column 4 is quite apparent. In Table V are given further data obtained by Cabannes for the relative scattering powers of a few other gases and vapours.

[1] Ann. d. Phys., *15*, 5 (1921).

TABLE V

Relative Scattering Powers of Gases and Vapours

Gas	Scattering power	Gas	Scattering power
H_2 ..	0·23	N_2O ..	3·8
A ..	0·8	Xe ..	5·5
O_2 ..	0·9	C_2H_6 ..	6·3
Air ..	1·0	C_3H_8 ..	12
N_2 ..	1·0	C_2H_5Cl ..	16
Kr ..	2·0	C_4H_{10} ..	22
CH_4 ..	2·4	$(C_2H_5)_2O$ ..	26
CO_2 ..	2·6		

The comparatively large scattering power exhibited by the organic vapours is consistent with the fact that they usually possess high refractivities.

√ *Absolute Scattering Power of a Gas and the Determination of the Avogadro Number.*—We have already seen (equation 29 of chapter III) that for a gas

$$\frac{I}{I_0}r^2 = \frac{\pi^2(n^2-1)^2}{2\nu\lambda^4}\left(\frac{6+6\varrho}{6-7\varrho}\right). \quad \ldots \quad \ldots \quad (3)$$

$\frac{I}{I_0}$ is a measure of the intensity of the light scattered per unit volume of the gas when expressed as a fraction of the intensity of the incident unpolarized light. ϱ is the depolarization of the light scattered in the transverse direction. If $\frac{I}{I_0}$ is measured experimentally, knowing other quantities involved in the equation, ν may be evaluated, and hence the Avogadro number. The earliest attempts in this direction were those of Cabannes[1], who chose argon for the purpose of the above measurements. A known length of the gas column is illuminated and the light emitted in a direction normal to the direction of illumination by a unit area of the surface is compared with the incident light. In the case of argon ($\varrho = 0$), the above equation reduces to (3*a*).

$$\frac{I}{I_0}r^2 = \frac{\pi^2(n^2-1)^2}{2\nu\lambda^4}. \quad \ldots \quad \ldots \quad \ldots \quad (3a)$$

[1] Ann. d. Phys., *15*, 5 (1921).

Cabannes obtained a value of $1{\cdot}34\times10^{-8}$ for $\frac{I}{I_0}r^2$ using $\lambda4358$ radiation. The gas investigated was a mixture of 91% argon, 8·7% nitrogen and 0·3% oxygen at normal pressure and a temperature of 27°C. After applying the necessary corrections for the impurities, he obtained $3{\cdot}08\times10^{19}$ for ν at N.T.P. This corresponds to a value of $6{\cdot}90\times10^{23}$ for the Avogadro number.

The next measurements were those of Daure[1], who used ethyl chloride vapour as the scattering substance. The experimental technique adopted by him is diagrammatically represented in Fig. 14.

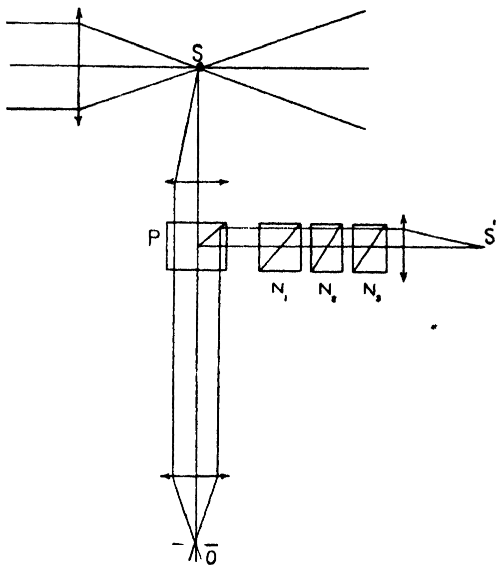


FIG. 14.

S is situated in a suitable tube of ethyl chloride vapour into which a beam of sun-light is focussed. The scattered light passes through a Lummer cube P and is compared with the light coming from an auxiliary source S′. The light from S′ is reduced to a desired fraction by the help of 3 nicols N_1, N_2 and N_3. In order to obtain the intensity of the source itself, a total

[1] Comptes Rendus, *180*, 2032 (1925).

reflection prism is kept at S and the experiment repeated. In this manner, the ratio of intensities of the scattered and the incident beams is measured. He obtained a value of $1{\cdot}06\times10^{-7}$ for $\frac{I}{I_0}r^2$ in this substance. The working temperature and pressure of ethyl chloride were 19°C. and 75 cm. of mercury respectively. In calculating the Avogadro number from these data, use is made of the more general form[1] of (3), namely,

$$\frac{I}{I_0}r^2 = \frac{\pi^2(n^2-1)^2}{2\lambda^4}\left(\frac{6+6\varrho}{6-7\varrho}\right)\cdot\frac{RT\beta}{N},$$

and ϱ is assumed to be equal to 0·016. Daure employed a composite radiation extending from λ5200 to 5700 A.U. for illuminating purposes and took account of it in the calculations. In this manner, he obtained a value of $6{\cdot}50\times10^{23}$ for the Avogadro number.

[1] See equation (16) of chapter V.

CHAPTER V

THEORY OF LIGHT SCATTERING BY DENSE MEDIA

✓ *Introduction.*—From the point of view of light scattering, a dense medium, such as is found in a liquid or a solid, differs from a gas at ordinary pressures in several important respects. The thermal movements of the constituent parts are no longer independent and we are not justified in assuming that the expectation of intensity in any direction is n times that due to a single centre, where n is the total number of centres. Destructive interference is bound to set in and the compounding of the amplitudes from various bits has to be effected with due regard to this possibility. In fact, it has already been shown that destructive interference is actually complete and that there will be no residual lateral emission, if ideal conditions prevail and any possibility of obtaining a residual effect rests on the fact that the actual conditions in a dense medium necessarily fall short, though only to a small extent, of such an ideal. In solving this problem of evaluating the aggregate scattering effect, we may either altogether disregard the structure of the medium and look upon it as an elastic continuum, or view it as an assembly of individual dielectric spheres or molecules either located at definite positions or moving about in accordance with the laws of kinetic theory. In either case, it is easy to see that the thermodynamical properties of the medium as a whole are unchanged at a given temperature. This statement, when applied to small bits of the medium, is true only in a statistical sense. Local fluctuations of the thermodynamical properties about their mean values are to be expected and we shall presently show that such fluctuations furnish a measure of the intensity of scattering.

The Medium regarded as a Continuum.—We shall first adopt the continuum view point and derive an expression for the intensity of the scattered light. If a given volume element V has a mean dielectric constant ε, which attains an instantaneous value $\varepsilon+\triangle\varepsilon$ as a result of fluctuation, it is easily seen that the

change in the induced optic moment is $\frac{\triangle\varepsilon}{4\pi}$ per unit volume per unit incident electric field. Substituting $\frac{\triangle\varepsilon}{4\pi}.V$, which represents the total increase in the optic moment, for $E_0\alpha$ in equation (1) of chapter III, we obtain expression (1) for the intensity of the instantaneous scattering in a transverse direction from the given volume element V.

$$\frac{(2\pi\nu)^4}{8\pi c^3 r^2}\left(\frac{\triangle\varepsilon}{4\pi}.V\right)^2 \quad .. \quad .. \quad .. \quad (1)$$

By dividing (1) with $\frac{c}{8\pi}$, we can express this scattered energy as a fraction of the incident energy. If the incident light is unpolarized, the total energy in the incident beam is doubled without any corresponding increase in the intensity of transverse scattering for reasons already explained. We therefore obtain expression (2) for the intensity of light scattered at a particular instant by the volume element V in a transverse direction, when expressed as a fraction of the incident energy, for unpolarized incident light.

$$\frac{\pi^2 V^2}{2\lambda^4 r^2}(\triangle\varepsilon)^2 \quad .. \quad .. \quad .. \quad (2)$$

The whole medium may be split up into a large number of such volume elements, each of which has a volume V and density σ. If the fluctuations in each volume element take place independently of those occurring in the neighbouring ones, we may regard the secondary radiations coming from the different volume elements as incoherent. The process of obtaining the average effect from all the volume elements at a given instant is equivalent to obtaining the average effect from a given volume element over a sufficiently long time and the result may be expressed by (2*a*).

$$\frac{\pi^2 V^2}{2\lambda^4 r^2}\overline{(\triangle\varepsilon)^2} \quad .. \quad .. \quad .. \quad (2a)$$

If $\triangle V$ and $\triangle\sigma$ represent the fluctuations in the volume and density respectively at any instant, we have

$$\frac{\overline{(\triangle\sigma)^2}}{\sigma^2} = \frac{\overline{(\triangle V)^2}}{V^2} \text{ because } \sigma V \text{ is a constant.}$$

Since [1] $$\overline{(\triangle V)^2} = -KT\left(\frac{\partial V}{\partial p}\right)_T,$$

we have

$$\frac{\overline{(\triangle \sigma)^2}}{\sigma^2} = -\frac{RT}{NV^2}\left(\frac{\partial V}{\partial p}\right)_T = \frac{RT\beta}{NV}, \quad \ldots \quad \ldots \quad (3)$$

where β stands for the isothermal compressibility of the medium. Differentiating the Clausius-Mosotti relation $\frac{\varepsilon-1}{\varepsilon+2} = c\,.\,\sigma$ and taking the time averages of both sides, we have

$$\overline{(\triangle \varepsilon)^2} = \frac{(\varepsilon-1)^2\,(\varepsilon+2)^2}{9}\cdot\frac{\overline{(\triangle \sigma)^2}}{\sigma^2}. \quad \ldots \quad \ldots \quad (4)$$

Substituting from (3) in (4), we obtain

$$\overline{(\triangle \varepsilon)^2} = \frac{RT\beta\,(\varepsilon-1)^2\,(\varepsilon+2)^2}{9NV}. \quad \ldots \quad \ldots \quad (5)$$

Combining (5) with (2*a*) and writing n^2 in the place of ε, we obtain (6) for the intensity of the light scattered per unit volume of a continuous medium, in the transverse direction.

$$\frac{I}{I_0} = \frac{\pi^2 RT\beta\,(n^2-1)^2\,(n^2+2)^2}{18\lambda^4 r^2 N}. \quad \ldots \quad \ldots \quad (6)$$

I and I_0 stand respectively for the intensities of the scattered and incident beams.

Validity of Clausius-Mosotti Relation.—It is well known that the factor $\varepsilon+2$ enters the Clausius-Mosotti relation when we consider the polarization field [2] of the medium as a whole. The appropriateness of using this relation, when we are dealing with the properties of small volume elements, has been questioned by Ramanathan. He has suggested that the relation $\varepsilon-1 = c\sigma$ is the proper one to be used and not the Clausius-Mosotti relation. It is argued that the factor $\varepsilon+2$ arises from the presence of the surrounding medium, the properties of which do not undergo changes consequent on the fluctuations within the small volume element and has therefore to be regarded as a

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[1] See (9) of Appendix III.

[2] The origin of the polarization field will be discussed in greater detail in a following section.

constant. Using the alternative relation and by following exactly the same procedure as before, we arrive at expression (6*a*) in the place of 6. The latter differs from the former in not having a factor $\frac{(n^2+2)^2}{9}$.

$$\frac{I}{I_0} = \frac{\pi^2 RT\beta (n^2-1)^2}{2\lambda^4 r^2 N} \quad \ldots \quad \ldots \quad \ldots \quad (6a)$$

The Medium regarded as an Assembly of Molecules.—The treatment outlined in the foregoing sections may be pushed further so as to include the anisotropic scattering also. The results obtained are identical with those that may be derived by taking the molecular structure of the medium into consideration. As the latter method is more directly related to some of the important properties of the individual molecules, we shall adopt it in the following.

The molecules in a crystal, for example, are by no means absolutely fixed. They are oscillating about certain mean positions and these oscillations are known to contribute to the specific heat of a crystal and also to affect the X-ray patterns. On account of these motions, there is not the absolute certainty of finding, for every molecule of the crystal, always another, the scattered beam from which will destroy that from the former. This element of randomness or lack of co-ordination in the movements of the molecules is responsible for a finite scattering. The randomness of movements of molecules may be expected to manifest itself even to a larger extent in the case of liquids. Precisely the same arguments as in the case of solids will show that the light scattered from various volume elements, so far as it depends on the average number of molecules in each element which determines the average density, will have the same amplitude for the various elements and in this respect the liquid is just like an ideal solid. The aggregate effect on this score will therefore vanish. On the other hand, the fluctuations in number will result in fluctuations in density and the total amplitude from any one element will generally differ from that obtained in any other at a given instant. A finite scattering, which may be termed *scattering due to fluctuations in density*, will result. In

addition to such fluctuations, we have also to reckon the possibility of the molecule being asymmetric and as such there will be fluctuations in orientation. At any given instant of time, the state of a particular volume element, with regard to the orientations of the different molecules in it, may not be exactly the same as that of another. This will result in the total amplitudes arising from the two elements being different irrespective of their instantaneous densities being equal or not. On this score also, there will result a certain amount of scattering, which may be termed *scattering due to fluctuations in orientation.* This is analogous to the part arising from the optical anisotropy of molecules in the case of gases and will likewise vanish, if the molecules of the liquid are spherical. Under such conditions, the state of any one volume element will not differ from any other merely on account of different orientations of the constituent molecules.

Detailed Theory of Light Scattering in Liquids.—Let the molecules of the liquid under consideration be optically anisotropic, the polarizabilities along the three principal directions in the free state being given as A, B and C. The corresponding effective polarizabilities in the liquid state may be represented by A′, B′ and C′. We may divide the liquid medium into a large number of volume elements whose linear dimensions are small in comparison with the wave-length of light but yet large enough for each volume element to contain an appreciable number of molecules. If we concentrate our attention on the state of any particular volume element, owing to thermal motions, there will be fluctuations in the number as well as the orientations of the molecules contained in it. The following remarks may now be made regarding the fundamental assumptions underlying the treatment.

1. The linear dimensions of the volume elements are small in comparison with the wave-length of light. We can therefore consider the waves scattered by different molecules in a given volume element to be optically coherent.

2. The volume elements are large enough to contain an appreciable number of molecules. Consequently, fluctuations in number taking place in a given volume element may be taken

to be uncorrelated with the fluctuations taking place in any other neighbouring volume element.[1]

3. The effect of close packing in liquids will be assumed not to interfere with the freedom of orientation of the molecules. The number of molecules in a given volume element, having a given orientation at an instant of time, will therefore be the same as though all the molecules in the volume element are oriented entirely at random. The fluctuations in orientation occurring in the different volume elements will entirely be uncorrelated with one another[2] and we may further assume that these are also uncorrelated with the fluctuations in density.

4. The fluctuations in number in an element of volume V are given by the Smoluchowski-Einstein expression

$$\overline{(\triangle \nu)^2} = \frac{RT\beta\nu^2}{NV}, \quad \ldots \quad \ldots \quad \ldots \quad (7)$$

where $\overline{(\triangle \nu)^2}$ is the mean square of the deviation of the number of molecules per unit volume from its mean value ν (see 10 of Appendix III). R, N, β and T are the gas constant, the Avogadro number, the isothermal compressibility and the absolute temperature respectively.

The procedure is now exactly similar to that adopted in the case of gaseous molecules except that we have A′, B′ and C′, the effective polarizabilities instead of A, B and C. Let a beam of plane polarized light be incident in the medium in the direction OY (Fig. 5). We shall examine the simple case where the electric vector E is confined to the direction OZ only. Let us consider the radiation from a particular molecule whose principal axes of polarizability have the co-ordinates θ, φ and ψ. If the effective optical polarizabilities are A′, B′ and C′, we have already seen that the moment p_z induced in the direction OZ is given by

$$p_z = E\,(A' \sin^2\theta \cos^2\psi + B' \sin^2\theta \sin^2\psi + C' \cos^2\theta).$$

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[1] A fuller discussion of this aspect is given by Ramanathan, Ind. Jour. Phys., *1*, 413 (1927).

[2] A possible correlation between such fluctuations in the neighbouring volume elements and its effect on the results have recently been considered by Mueller, Proc. Roy. Soc., *166*, 425 (1938).

p_y, the moment induced in the direction OY, may be written as

$$p_y = E(-A' \sin\theta \cos\psi \sin\psi \cos\varphi - A' \sin\theta \cos^2\psi \sin\varphi \cos\theta + B' \sin\theta \sin\psi \cos\psi \cos\varphi - B' \sin\theta \cos\theta \sin^2\psi \sin\varphi + C' \sin\theta \cos\theta \sin\varphi).$$

At a distance r, in a direction transverse to both OY and OZ, the effect of these induced moments is to give a scattered beam of amplitude $\frac{4\pi^2}{r\lambda^2} p_z$ parallel to OZ and $\frac{4\pi^2}{r\lambda^2} p_y$ parallel to OY (see equation 3 of chapter III). It has already been remarked that the radiations from different molecules in a given volume element are all coherent and in order to get their instantaneous aggregate effect, we merely have to sum up their respective amplitudes. Thus, the amplitude Y at any given instant, of the Y component of the radiation from a particular volume element will be given by

$$Y = \frac{4\pi^2}{r\lambda^2} \Sigma p_y .$$

Σ denotes summation over all the molecules in V, whose total number is equal to νV. When we come to the question of compounding the effect from the different volume elements, it must be remembered that the chance orientations of the molecules in any one volume element at a particular instant of time are quite uncorrelated with those obtained in any other at that instant. If the summation of terms like $\frac{4\pi^2}{r\lambda^2} \Sigma p_y$ is carried over a sufficiently large number of volume elements at any instant of time, the result will be zero as this process is equivalent to summing up p_y over all possible values of θ, φ and ψ. In other words, Σp_y will be as often positive as negative at any given instant of time if we consider a large number of volume elements. The aggregate effect should however be obtained by adding up the squares of the amplitudes and not the amplitudes themselves as the radiations from different volume elements are incoherent. Thus in order to obtain the intensity of scattering by a given volume V, we have to find the average of $\left[\frac{4\pi^2}{r\lambda^2} \Sigma p_y\right]^2$ over all the volume elements. This process is

identical with that of finding the average of this term from the same volume element over a sufficiently long interval of time. Since we have assumed that there is perfect freedom of orientation for each of the molecules, they will take up all possible values of θ, φ and ψ during this long interval of time. When the averaging is performed under such conditions, all the cross products vanish and it may easily be shown that $\left(\frac{4\pi^2}{r\lambda^2}\right)^2 \overline{p_y^2}$ represents the effect per molecule. $\overline{p_y^2}$ is the time average of p_y^2. The averaging is carried out as before (see equation 20 of chapter III). Remembering that $E_z = E$, $E_x = E_y = 0$, we get the following equation in the place of (23) of chapter III.

$$\overline{p_y^2} = \frac{E^2}{15}\left\{A'^2 + B'^2 + C'^2 - A'B' - B'C' - C'A'\right\} = \frac{E^2\gamma'^2}{15}.$$

The intensity of the Y component of the scattered beam per unit volume is therefore given by

$$I_y = \frac{16\pi^4}{r^2\lambda^4}\nu E^2 . \frac{\gamma'^2}{15}. \quad \cdots \quad \cdots \quad (8)$$

Similarly we have $\frac{4\pi^2}{r\lambda^2}\Sigma p_z$ for the amplitude of the Z component from a particular volume element, where

$$\Sigma p_z = E\Sigma\,(A' \sin^2\theta \cos^2\psi + B' \sin^2\theta \sin^2\psi + C' \cos^2\theta).$$

The summation extends over all the molecules in the given volume element. Denoting this amplitude by Z, we can rewrite its instantaneous value in the form

$$Z = \frac{4\pi^2}{r\lambda^2}E\left[\Sigma\frac{A'+B'+C'}{3} + \Sigma\left(L - \frac{A'+B'+C'}{3}\right)\right]$$

$$= \frac{4\pi^2}{r\lambda^2}E(\nu + \triangle\nu)V\alpha' + \frac{4\pi^2}{r\lambda^2}E\Sigma(L-\alpha'). \quad \cdots \quad \cdots \quad (9)$$

L in (9) stands for the function $A' \sin^2\theta \cos^2\psi + B' \sin^2\theta \sin^2\psi + C' \cos^2\theta$. The first term may be denoted by Z_1 and the second by Z_2. The latter is easily seen to be closely analogous to the Y component of the amplitude with which we have already dealt. Its value for any particular element is finite and is either positive or negative at a given instant according

to the particular chance orientation taken up by the molecules of the element under question at that instant. When the summation is extended as such to all the volume elements, the aggregate amplitude vanishes. It has, however, been remarked that so far as the different volume elements are concerned, we have to regard both the density and orientation scattering coming from them as incoherent. Hence, in order to get the aggregate effect, we have to find the average value of the square of this term for all the volume elements, which process is identical with that of finding the time average value of its square for the same element. As before, this average will be represented by $\overline{Z_2^2} = \left(\frac{4\pi^2}{r\lambda^2}\right)^2 E^2\,\overline{(L-\alpha')^2}$ per molecule, where $\overline{(L-\alpha')^2}$ is the time average of $(L-\alpha')^2$.

But $\overline{(L-\alpha')^2} =$

$$\frac{\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi} [(A'\sin^2\theta\cos^2\psi + B'\sin^2\theta\sin^2\psi + C'\cos^2\theta) - \alpha']^2 \sin\theta\, d\theta d\varphi d\psi}{\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi} \sin\theta\, d\theta d\varphi d\psi}$$

$$= \tfrac{4}{45}(A'^2 + B'^2 + C'^2 - A'B' - B'C' - A'C') = \tfrac{4}{45}\gamma'^2.$$

The intensity of the second part of the Z component of the scattered beam per unit volume, which may be denoted by I_{z_2}, is therefore given by

$$I_{z_2} = \frac{16\pi^4}{r^2\lambda^4}\nu E^2 \,.\, \tfrac{4}{45}\gamma'^2. \quad \ldots \quad \ldots \quad \ldots \quad (10)$$

Now we consider the first term Z_1 of (9). If we regard the average effective polarizability α' as independent of the fluctuation in density, we may split up Z_1 into two terms and write

$$Z_1 = \frac{4\pi^2}{r\lambda^2} E\alpha'\nu V + \frac{4\pi^2}{r\lambda^2} E\alpha'\triangle\nu V.$$

The first term represents that part of the amplitude whose magnitude is independent of the particular volume element under consideration. So far as this term is concerned, the compounding of the amplitudes for various volume elements will

therefore result in a zero amplitude on account of the regularity of arrangement in the volume elements. The second term depends, however, on the existence of an instantaneous fluctuation $\triangle\nu$ and as these fluctuations take place independently of each other in the different elements, the aggregate intensity will be proportional to the sum of the squares of such terms. The average effect from each volume element will be

$$\left(\frac{4\pi^2}{r\lambda^2}\right)^2 E^2\alpha'^2\,\overline{(\triangle\nu)^2}\,V^2.$$

Substituting the Einstein-Smoluchowski expression for $\overline{(\triangle\nu)^2}$ from (7) and using the relation $\nu\alpha' = \frac{n^2-1}{4\pi}$, we obtain the intensity of density scattering from each volume element as

$$\left(\frac{4\pi^2}{r\lambda^2}\right)^2 E^2.\,\frac{RT\beta}{N}.\left(\frac{n^2-1}{4\pi}\right)^2 V.$$

The intensity of scattering I_{z_1} per unit volume will be given by

$$I_{z_1} = \frac{16\pi^4}{r^2\lambda^4}.\,E^2.\,\frac{RT\beta}{N}.\left(\frac{n^2-1}{4\pi}\right)^2. \qquad \ldots \qquad \ldots \quad (11)$$

The total intensity of the Z component is the sum of the expressions (10) and (11) and is given by (12).

$$I_z = \frac{16\pi^4}{r^2\lambda^4}E^2\nu\left[\frac{RT\beta\nu}{N}\left(\frac{n^2-1}{4\pi\nu}\right)^2 + \tfrac{4}{45}\,\gamma'^2\right]. \qquad \ldots \quad (12)$$

The depolarization of the scattered light is easily seen to be given by (13).

$$\varrho_v = \frac{I_y}{I_z} = \frac{\gamma'^2/15}{\frac{RT\beta\nu}{N}\left(\frac{n^2-1}{4\pi\nu}\right)^2 + \frac{4}{45}\gamma'^2}. \qquad \ldots \qquad \ldots \quad (13)$$

If the incident light is unpolarized instead of being plane polarized, it is easily seen that an additional term equal to I_y is added to both the Y and Z components and we have (14) for ϱ_{liq}

$$\varrho_{liq.} = \frac{2I_y}{I_z+I_y} = \frac{\frac{2}{15}\gamma'^2}{\frac{RT\beta\nu}{N}\left(\frac{n^2-1}{4\pi\nu}\right)^2 + \frac{7}{45}\gamma'^2}. \qquad \ldots \quad (14)$$

Substituting α' for $\dfrac{n^2-1}{4\pi\nu}$ in (14), we may write

$$\varrho_{\text{liq}} = \frac{\frac{6}{45}\gamma'^2}{\frac{\text{RT}\beta\nu}{\text{N}}\alpha'^2+\frac{7}{45}\gamma'^2} = \frac{6\delta_{\text{liq.}}}{\frac{5\text{RT}\beta\nu}{\text{N}}+7\delta_{\text{liq.}}} \quad \ldots \quad (15)$$

This is analogous to (2) of chapter IV. Alternatively, we have

$$\delta_{\text{liq.}} = \frac{5\text{RT}\beta\nu}{\text{N}}\cdot\frac{\varrho_{\text{liq}}}{6-7\varrho_{\text{liq}}}.$$

The total intensity of the light scattered per unit volume is equal to $3\text{I}_y+\text{I}_z$ and this may be written as

$$3\text{I}_y+\text{I}_z = \frac{16\pi^4}{r^2\lambda^4}\text{E}^2\nu\,.\,\frac{\text{RT}\beta\nu}{\text{N}}\,\alpha'^2\left[1+\frac{13\varrho_{\text{liq}}}{6-7\varrho_{\text{liq}}}\right],$$

whereas the intensity of the incident light on this scale is equal to 2E^2. We therefore have

$$\frac{\text{I}_{\text{liq.}}}{\text{I}_0} = \frac{8\pi^4}{r^2\lambda^4}\frac{\text{RT}\beta\nu^2}{\text{N}}\,\alpha'^2\left(\frac{6+6\varrho_{\text{liq.}}}{6-7\varrho_{\text{liq.}}}\right)$$

$$= \frac{8\pi^4}{r^2\lambda^4}\cdot\frac{\text{RT}\beta}{\text{N}}\left(\frac{n^2-1}{4\pi}\right)^2\left(\frac{6+6\varrho_{\text{liq.}}}{6-7\varrho_{\text{liq.}}}\right). \quad \ldots \quad (16)$$

Expressions (15) and (16) readily reduce to equations (25*a*) and (29) respectively of chapter III obtained in the case of gases, if the compressibility β is put equal to $\frac{1}{p}$ or $\frac{\text{N}}{\text{RT}\nu}$. (15) and (16) are therefore only to be regarded as more general forms of (25*a*) and (29) of chapter III. It may also be noted that if $\varrho_{\text{liq.}}$ is put equal to zero, equation (16) reduces to (6*a*) as it ought to. α' and γ' are the effective mean polarizability and the effective anisotropy respectively of the molecule in the liquid state and these may differ appreciably from α and γ. ϱ in this case is, of course, the depolarization observed in the liquid state.

A few remarks may not be out of place here regarding the validity of the fundamental assumptions outlined in the beginning of this section. Assumptions 2 and 4 are somewhat of a general nature and may not be far from the actual state of affairs that

prevail in a liquid. Recent experimental evidence appears, however, to call into question the validity of assumption 3. As an example, we may cite the case of rotational Raman effect. The postulated presence of complete freedom of orientation of the molecules in a liquid should result in rotational Raman spectra which possess the same characteristic features as are obtained in a gas. Experiments do not support this conclusion.[1]

Evaluation of the Effective Moments in a Liquid.—Since all the molecules of the medium behave as dipoles under the action of incident light, the field acting on any one of them will not be identical with the external field. If E is the external field acting, the displacement D inside a dielectric is given by

$$\mathrm{D} = \mathrm{E}+4\pi\mathrm{P}$$

where P stands for the dielectric polarization or the optic moment induced per unit volume of the material. This may be written as $\nu\alpha\mathrm{E}'$, where E' is the effective field acting on each molecule, ν is the number of molecules per c.c. and α the polarizability of each molecule. Dividing throughout by E and substituting ε, the dielectric constant of the medium, for $\frac{\mathrm{D}}{\mathrm{E}}$, we have $\frac{\varepsilon-1}{4\pi}=\frac{n^2-1}{4\pi}=\frac{\nu\alpha\mathrm{E}'}{\mathrm{E}}$. If we denote $\frac{\alpha\mathrm{E}'}{\mathrm{E}}$ by a new symbol α' which we may call the effective polarizability of the molecule, we have the following very general equation.

$$\frac{n^2-1}{4\pi} = \nu\alpha' \qquad \ldots \quad \ldots \quad \ldots \quad (17)$$

The relationship between E and E' and therefore between α and α' depends, however, on the nature of the dielectric medium and may be deduced from the following considerations. Every molecule is surrounded by polarizable matter which would therefore acquire a dipole moment under the action of the external field. These dipoles will also produce an additional component at the molecule under consideration besides the external field E. The resultant field may be evaluated by making certain simplifying assumptions. If a small sphere is

[1] See papers by Bhagavantam and A. V. Rao in the Proceedings of the Indian Academy of Sciences.

described round the molecule in question, the total field produced may be regarded as consisting of the three following parts:—

1. The External field E.
2. The field at the centre of the sphere due to the induced moments outside the sphere. This is equal to $\frac{4\pi P}{3}$ where P is the moment induced per unit volume.[1]
3. The field at the centre due to the moments induced in the molecules lying within the sphere. This term vanishes in case the distribution of the polarizable matter within the sphere possesses cubic symmetry.[2]

Thus in a simple case, the polarization field is equal to $\frac{4\pi P}{3}$ and this is usually referred to as the Lorentz-Lorenz polarization field. It leads to the well-known law of refraction named after these authors. We have

$$E' = E+\frac{4\pi P}{3} \quad \text{or} \quad \frac{E'}{E} = 1+\frac{4\pi\chi}{3}$$

where χ is the moment induced per unit volume per unit external field. It follows that

$$\alpha' = \alpha\left(1+\frac{4\pi\chi}{3}\right).$$

In the case of media like gases, χ is very small and α' does not differ appreciably from α and for all practical purposes both may be taken as identical. Hence no distinction was made between the effective polarizability and the actual polarizability in the earlier chapters as we were then dealing with gaseous media only. In dense media like liquids, χ is appreciable and α' is quite different from α. Incidentally we may note that

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[1] This is a well-known theorem and is proved in any text book dealing with dielectric polarization.

[2] In a general case, such as the one in which the distribution is of an unsymmetrical type, statements 2 and 3 are not valid.

since, χ, the moment induced per unit volume per unit external field, is $\nu\alpha'$ which is equal to $\frac{n^2-1}{4\pi}$, we have

$$\alpha' = \alpha\left(\frac{n^2+2}{3}\right).$$

Substitution of this in equation (17) leads to

$$\frac{n^2-1}{n^2+2} = \frac{4\pi\nu\alpha}{3} \quad \text{or} \quad \frac{n^2-1}{n^2+2} \cdot \frac{M}{\sigma} \text{ is a constant.}$$

This is the well known Lorentz-Lorenz law of refraction. If we assume a polarization field of the Lorentz-Lorenz type to exist in the medium, we have the effective moments and the actual moments connected by equations of the type

$$A' = A\left(1+\frac{4\pi\chi}{3}\right) \text{ etc., where } \chi = \frac{n^2-1}{4\pi}.$$

In such a special case, it is easily seen that

$$\alpha' = \alpha\left(\frac{n^2+2}{3}\right) \text{ and } \gamma' = \gamma\left(\frac{n^2+2}{3}\right).$$

Consequently (15) reduces to (15*a*) and (16) remains unaltered.

$$\varrho_{\text{liq.}} = \frac{\frac{6}{45}\gamma^2}{\frac{RT\beta\nu}{N}\alpha^2+\frac{7}{45}\gamma^2} \quad \ldots \quad \ldots \quad (15a)$$

One of the most important consequences of the above expressions is the relationship between the values of ϱ obtained in the liquid and gaseous states of a particular substance. From the values given for $\varrho_{\text{liq.}}$ (15*a*) and for ϱ_{gas} (25*a* of chapter III), we may easily arrive at the relation (18).

$$\frac{RT\beta\nu}{N} \cdot \frac{\varrho_{\text{liq.}}}{6-7\varrho_{\text{liq}}} = \frac{\varrho_{\text{gas}}}{6-7\varrho_{\text{gas}}} \quad \ldots \quad \ldots \quad (18)$$

That the values calculated for ϱ_{liq} from eqn. (18) differ widely from the observed results was first pointed out by Raman and Krishnan.[1] The following Table taken from a paper by these authors illustrates the discrepancy.

[1] Phil. Mag., 5, 498 (1928).

TABLE VI

Relation between $\rho_{liq.}$ and ρ_{gas}

Substance	Dimensions of the molecule in A.U.		ρ_{gas} observed	$\rho_{liq.}$ calculated from		$\rho_{liq.}$ observed
	$\bar{a}$	$\bar{b} = \bar{c}$		Isotropic polarization field (18)	Anisotropic polarization field	
Pentane ..	8·7	4·9	0·013	0·21	0·074	0·075
Hexane ..	10·0	4·9	0·015	0·31	0·087	0·100
Heptane ..	11·3	4·9	0·016	0·38	0·083	0·100
Octane ..	12·6	4·9	0·018	0·46	0·105	0·130

With a view to explain these discrepancies, Raman and Krishnan have revised the above derivations by introducing an anisotropic polarization field instead of a Lorentz-Lorenz one. It has already been mentioned that the effective field E′ at a given molecule may be taken to be $E+\frac{4\pi P}{3}$, only if the molecules surrounding the same are distributed in such a manner as to be equivalent to a symmetrical distribution of polarizable matter. If the shape of the molecule departs greatly from spherical symmetry, it would be incorrect to regard the distribution of polarizable matter as conforming to the above arrangement. The polarization field acting on a molecule will neither be $\frac{4\pi P}{3}$ nor will it be the same in all directions. This anisotropy is expressed in the usual manner by an ellipsoid, the principal axes of which are taken for simplicity to coincide with those of the polarization ellipsoid. When the incident field acts along any one of these axes, the polarization field also is in the same direction and is given by $p_1\chi E$, $p_2\chi E$ and $p_3\chi E$, instead of $\frac{4\pi}{3}\chi E$ in each case. p_1, p_2 and p_3 are coefficients characteristic of the molecule, and these generally differ from $\frac{4\pi}{3}$. These

coefficients need not be, and in general will not be, independent of temperature or the nature of aggregation in the medium. If A′, B′ and C′ are the effective principal polarizabilities, these will be related to the actual polarizabilities by relations like

$$A' = A(1+p_1\chi)\,;\ B' = B(1+p_2\chi)\ \ldots \text{ etc.} \qquad (19)$$

What has now been done is equivalent to describing an ellipsoidal cavity round the molecule under consideration instead of a spherical cavity as has been done by Lorentz, the medium being still regarded as continuous and isotropic.[1] Under such conditions, if we are dealing with the simple case of a spheroidal cavity, we may write

$$p_1 = 4\pi\left(\frac{1}{e^2}-1\right)\left(\frac{1}{2e}\log\frac{1+e}{1-e}-1\right)$$

$$p_2 = p_3 = 2\pi\left(\frac{1}{e^2}-\frac{1-e^2}{2e^3}\log\frac{1+e}{1-e}\right) \qquad (20)$$

where e is given by $\bar{b} = \bar{c} = \bar{a}\,(\sqrt{1-e^2})$. $\bar{a}$, $\bar{b}$ and $\bar{c}$ represent the dimensions of the molecule and may be taken as the axes of the cavity. In the general case p_1, p_2 and p_3 will be given by

$$p = 2\pi\,\bar{a}\,\bar{b}\,\bar{c}\int_0^\infty \frac{dw}{(m^2+w)\sqrt{(\bar{a}^2+w)(\bar{b}^2+w)(\bar{c}^2+w)}}$$

where m may stand for $\bar{a}$, $\bar{b}$ or $\bar{c}$ as the case may be. The values calculated by Raman and Krishnan in this manner using eqns. (18), (19) and (20) for four liquids are given in Table VI for comparison with the observed values and the values calculated

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[1] It is doubtful if the medium surrounding an ellipsoidal cavity described about a single molecule may be regarded as continuous. Moreover, this theory does not explicitly take into account the two widely accepted notions about the liquid state relating to the formations of temporary groups of molecules and the hindered nature of the rotatory movements of the individual molecules. These and other defects of the theory have been pointed out by a number of workers and amongst the recent attempts to furnish a more logical picture of the optics of the liquid state, mention may be made of Hans Mueller [Phys. Rev., *50*, 547 (1936)]. Nevertheless, the successes of the Raman-Krishnan hypothesis have been very numerous and varied.

on the assumption of an isotropic polarization field. Good agreement is to be noticed between the observed values and the values calculated by the introduction of an anisotropic polarization field.

Amorphous Solids.—Under the class of amorphous solids are to be considered the large group of optical glasses, transparent jellies, and other supercooled liquids.[1] Experimental work in this direction has been somewhat scanty, owing to the obvious difficulty of obtaining these substances totally free from inclusions of air. An amorphous solid is essentially different from a crystal but resembles a liquid more, in that the atoms in it are not similarly oriented and do not occupy fixed and definite positions as in a crystal lattice. The absence of double refraction in an amorphous substance and the close similarity between the X-ray diffraction photographs obtained in them and those obtained in liquids constitute ample evidence in favour of the above view. Thus the system, although named an amorphous *solid,* is more like a *liquid* than a solid with the exception that the movements of the molecules constituting the amorphous medium may be somewhat sluggish in comparison with those found in a liquid. In a liquid, a fluctuation in density on the positive side is always immediately accompanied by a fluctuation on the negative side and the time mean value of the fluctuation is necessarily zero even for small volume elements. On the other hand, in amorphous solids, fluctuations of a quasi-permanent nature may have to be recognized. With this picture of the amorphous solid, we can easily see, by applying the same reasoning as in the case of a liquid, that the intensity of the light scattered by these bodies should be comparable with that obtained in liquids. That a large variety of optical glasses do exhibit scattered light of the requisite order of intensity obeying the usual laws of scattering has been shown experimentally by Raman.[2]

[1] Many organic liquids like molten salol, betol, etc., can be cooled into perfectly transparent glasses at liquid air temperatures and these are presumably amorphous.

[2] Jour. Opt. Soc. Amer., *15*, 185 (1927).

CHAPTER VI

EXPERIMENTAL RESULTS IN LIQUIDS AND COMPARISON WITH THEORY

Checking the Theory and the Determination of Avogadro Number.—The earliest measurements in this direction were those of Lord Rayleigh[1]. He found that the light scattered by liquid ether was 64 times as strong as that scattered by ether vapour at a pressure of 39 cm. and a temperature of 21°C. The liquid under these conditions is about 446 times as dense as the vapour. The scattering power, molecule per molecule, is therefore diminished seven times in the liquid state. This result is in full conformity with the later developments of the subject, already discussed in chapter V, dealing with the theory of light scattering by dense media. Subsequent investigations of Raman and Rao[2] on water have also shown that the absolute scattering power of liquids is much smaller than that of the corresponding vapours. Apart from such a qualitative confirmation of the theory in liquids, there is the important question of deciding whether or not the expressions derived in chapter V (16 in particular) are in quantitative agreement with the experimental results obtained in dense media. The various points that lend support to expression (16) are set out below. Most of the work in this direction is due to Martin and Lehrman,[3] Raman and Rao,[4] Krishnan,[5] Cabannes and Daure[6] and Rao.[7]

Krishnan critically examined all the available data up to 1926 and showed that the relative measurements of intensity in a large number of organic liquids entirely support expression (16).

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[1] Proc. Roy. Soc., *95*, 155 (1918).

[2] *Molecular Diffraction of Light* (1922).

[3] Jour. Phys. Chem., *24*, 478 (1920), and *26*, 75 (1922).

[4] Phil. Mag., *45*, 625 (1923).

[5] *Ibid.*, *50*, 697 (1925).

[6] Comptes Rendus, *184*, 520 (1927).

[7] Ind. Jour. Phys., *2*, 7 (1927).

Table XI reproduces the results of calculations based on (16) along with the observed intensities in some typical liquids. The compressibilities are all taken from Tyrer [1], Dakshinamurti [2] and Philip [3].

Martin, Raman and Rao, Martin and Lehrman, Cabannes and Daure, and Cabannes had carried out experiments on the measurement of absolute intensity of the scattered light in water, ether and benzene. Peyrot [4] has recently obtained the absolute intensity of the scattered light in benzene again. The relevant results are given in Table VII.

TABLE VII

Determination of the Avogadro Number

Substance	Author	Intensity $\frac{I}{I_0} \cdot r^2 \cdot 10^6$	Values assumed for the various constants occurring in (16) $\lambda \times 10^8$	n	$\beta \times 10^{12}$	T	ρ_{liq}	$R \times 10^{-7}$	Avogadro number calculated from (16)
Water ..	*M*	2·0	4358	1·3388	47·2	305	0·096	8·308	$6 \cdot 4 \times 10^{23}$
Ether ..	*M & L*	9·2	4861	1·352	209	303	0·085	,,	$4 \cdot 2 \times 10^{23}$
Benzene	*C & D*	10·7	5440	1·508	88	288	0·42	,,	$5 \cdot 0 \times 10^{23}$
,, ..	*P*	34·8	4358	1·524	97·4	297	0·42	,,	$4 \cdot 6 \times 10^{23}$

The Avogadro number, calculated with the help of (16) of chapter V in each case, is given in the last column. The order of magnitude is correct although the agreement is not as good as one would expect it to be.

Ramachandra Rao measured the intensity of light scattering at different temperatures for a very large number of liquids. Complete data on compressibility are available for three different liquids over the entire ranges studied and only in part for nine other liquids. The values calculated on the basis of expression (16), along with the observed ones in the three liquids for which data are available, are given in the following Tables. The general agreement between the calculated and the observed values lends strong support to the validity of expression (16).

[1] Jour. Chem. Soc., *105*, 2534 (1914).

[2] Proc. Ind. Acad. Sci., *5*, 385 (1937).

[3] *Ibid.*, *9*, 109 (1939).

[4] Comptes Rendus, *203*, 1512 (1936).

TABLE VIII

Isopentane

Temperature °C.	Observed value of ρ_{liq}	$\beta \times 10^6$ per atmosphere	I_t/I_{30} Observed	I_t/I_{30} Calculated
30	·056	238	1·00	1·00
60	·056	383	1·53	1·54
80	·053	474	1·76	1·78
90	·0516	580	2·16	2·15
100	·048	740	2·49	2·65
110	·047	907	2·97	3·09
120	·042	1090	3·35	3·53
130	·039	1430	3·98	4·16
140	·029	1956	5·61	5·44
150	·027	2626	6·80	6·87
160	·0215	3884	8·74	8·83
170	·018	12400	24·72	26·73
180	·015	43970	87·80	90·7

TABLE IX

Normal pentane

Temperature °C.	Observed value of $\rho_{liq.}$	$\beta \times 10^6$ per atmosphere	I_t/I_{30} Observed	I_t/I_{30} Calculated
30	·072	235	1·00	1·00
60	·072	437	1·76	1·76
80	·071	606	2·35	2·33
90	·065	706	2·60	2·61
100	·0576	830	2·97	2·95
110	·056	970	3·29	3·33
120	·050	1120	3·36	3·67
130	·040	1320	3·66	4·02
140	·034	1550	4·06	4·41
150	·0256	2130	4·92	5·53
160	·020	2980	6·60	7·02
170	·018	5030	9·28	10·63
180	·0157	9060	18·00	19·90
190	·0124	39800	60·00	62·10

TABLE X

Ethyl ether

Temperature °C.	Observed value of $\rho_{liq.}$	$\beta \times 10^6$ per atmosphere	I_t/I_{30} Observed	I_t/I_{30} Calculated
30	·080	212	1·00	1·00
50	·080	258	1·20	1·21
70	·076	323	1·40	1·42
100	·073	539	2·06	2·16
110	·0713	696	2·56	2·68
120	·070	880	2·99	3·22
130	·061	1140	3·86	3·77
140	·049	1700	4·76	5·29
150	·033	3280	8·30	9·30
160	·025	4660	10·80	11·80
170	·015	6500	13·80	14·30
180	·0124	11400	19·80	20·80
187	·0103	45000	60·00	62·50

Results Regarding the Depolarization and the Relative Intensities of the Light Scattered by Liquids.—Apart from the early work of Martin and Lehrman, and Raman and collaborators, the only systematic work done in this direction appears to be that of Krishnan, Banerjee and recently Peyrot. Some of their results, along with those of the earlier workers, are given below in Table XI. Only such liquids for which the isothermal compressibility is available from the work of Tyrer, Dakshinamurty or Philip are included in the Table. In all such cases, the intensity of the scattered light in relation to that of benzene has been calculated from the known densities and the refractive indices. Data regarding depolarization factors and intensities are available in several other liquids but these are not included here as they are usually quoted exhaustively in standard reference Tables. All the data in Table XI have been so chosen that they refer to temperatures as close to 30°C. as possible.

Experimental Technique.—The technique adopted by different authors for the measurement of depolarization of the scattered light is practically the same. The liquid is first purified by slow distillation in an evacuated bulb of the shape shown in

Fig. 15. The dust-free [1] liquid is collected into one of the bulbs, leaving the residue in the other. The bulb containing the distilled liquid is immersed in a rectangular bath of clear water in order to minimize any possible complications arising from the sphericity of the flask. Containers of alternative shapes such as cubical vessels have also been used. In such cases, the liquid has to be poured into the container after distillation, taking care to see that it catches no dust during this process. The incident light (either sun-light or arc-light [2]) is focussed by means of a long focus lens into the centre of the flask and

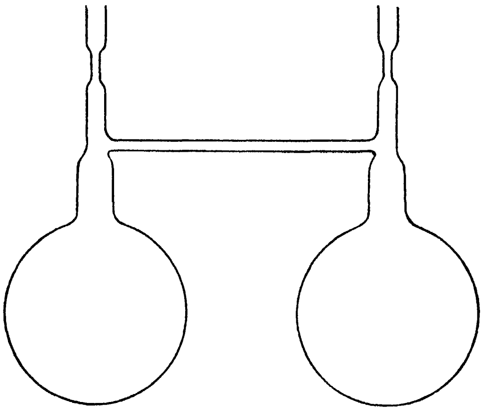


FIG. 15.

observations are made in a transverse direction. Observations should be confined to the focal plane, as far as possible, and a correction employed for convergence in the incident beam. Alternatively, a parallel beam obtained from a point source, placed at the focus of a good quality lens, may be used and the convergence correction dispensed with, since in liquids the scattering is ordinarily quite intense. The rest of the technique is exactly similar to that already described for gases. The

[1] It is of utmost importance that the liquids should be completely free from dust and other suspended particles in all experiments on light scattering, for obvious reasons.

[2] The relative merits of these sources have already been discussed.

TABLE XI

Depolarization and Relative Intensities of Scattered Light in Liquids *

Liquid	Formula	n	Density	$\beta \times 10^6$ per atm.	$\rho \times 100$	I obs. benzene = 3·15	I calc. from (16) benzene = 3·2	$\delta_{liq.} \times 10^3$ from (15)	References to columns 6 and 7†
Water ..	H_2O	1·333	0·996	44	8·8	0·17	0·25	4·9	7
Carbon disulphide	CS_2	1·656	1·248	95	62·0	13·0	13·4	72·4	6 & 1
Carbon tetra-chloride ..	CCl_4	1·468	1·575	114	6·0	1·02	1·38	1·6	4 & 1
Chloroform ..	$CHCl_3$	1·453	1·470	108	24·2	1·26	1·83	9·3	1
Methyl alcohol ..	CH_4O	1·334	0·783	131	4·9	0·46	0·67	3·5	7
Ethylene chloride	$C_2H_4Cl_2$	1·453	1·239	87	36·0	1·44	2·00	14·0	1
Ethyl bromide ..	C_2H_5Br	1·430	1·438	144	25·0	1·58	2·20	13·9	1
Ethyl alcohol ..	C_2H_6O	1·367	0·781	121	5·6	0·55	0·81	2·6	7
Acetic acid ..	$C_2H_4O_2$	1·376	1·040	99	38·7	0·95	1·58	25·1	7
Propyl alcohol ..	C_3H_8O	1·390	0·804	107	5·8	0·57	0·84	1·9	7
Isopropyl ,, ..	C_3H_8O	1·382	0·789	114	3·9	0·53	0·81	1·1	7
Acetone ..	C_3H_6O	1·369	0·791	113	25·0	0·81	1·21	11·3	5 & 1
Butyl alcohol ..	$C_4H_{10}O$	1·390	0·810	86	7·5	0·60	0·70	1·6	7
Acetic anhydride	$C_4H_6O_3$	1·395	1·067	89	43·0	1·01	1·81	16·6	1
Diethyl ether ..	$C_4H_{10}O$	1·352	0·702	212	8·0	1·00	1·37	3·7	5 & 1
Ethyl acetate ..	$C_4H_8O_2$	1·377	0·889	125	23·0	0·98	1·34	8·2	3 & 1
Amyl alcohol ..	$C_5H_{12}O$	1·397	0·803	91	8·0	0·74	0·78	1·5	5 & 1
Hexane ..	C_6H_{14}	1·372	0·653	159	9·95	1·00	1·22	2·8	3 & 1
Benzene ..	C_6H_6	1·495	0·868	95	42·0	3·15	3·20	18·0	7
Chlorobenzene ..	C_6H_5Cl	1·514	1·095	76	60	4·63	5·36	30·6	2
Aniline ..	$C_6H_5NH_2$	1·604	1·013	48	60	3·18	5·02	21·6	2
Nitrobenzene ..	$C_6H_5NO_2$	1·572	1·203	53	68·2	10·88	7·48	35·8	3 & 2
Heptane ..	C_7H_{16}	1·391	0·684	131	10·0	1·00	1·13	2·1	1
Anisol ..	C_7H_8O	1·508	0·983	63	50·0	3·52	2·92	14·3	1
Toluene ..	C_7H_8	1·509	0·856	97	48·0	3·53	4·21	20·4	7
Acetophenone ..	C_8H_8O	1·510	1·001	62	70·0	5·66	7·46	40·9	1
m-xylene ..	C_8H_{10}	1·511	0·856	91	50·6	4·10	4·36	18·8	7
Eucalyptus oil ..	..	1·455	0·919	89	36·0	1·38	2·06	..	8
Cajeputti ,, ..	..	1·462	0·905	84	32·3	1·38	1·83	..	8
Coriandri ,, ..	..	1·464	0·863	86	34·7	1·66	2·02	..	8
Anisi ,, ..	..	1·553	0·978	68	75·8	13·8	16·3	..	8
Citronellae ,, ..	..	1·467	0·841	79	34·7	3·2	1·88	..	8
Santali ,, ..	..	1·504	0·947	59	33·8	1·5	1·64	..	8
Ground-nut ,, ..	..	1·467	0·908	66	35·5	2·0	1·60	..	8

* The observations of Peyrot are with reference to benzene as one unit but they are given in the Table after reducing them to the scale of benzene = 3·15. Some of the results refer to white light and some to monochromatic light. The refractive indices in most cases refer to the F line and in a few cases to the D line. The small differences arising out of this are not very important.

† 1. K. S. Krishnan, Phil. Mag., *50*, 697 (1925).

2. A. N. Banerjee, Ind. Jour. Phys., *2*, 57 (1927).

3. J. Cabannes, La diff. Moleculaire de La Lumiere (1929).

4. S. Venkateswaran, Phil. Mag., *14*, 258 (1932).

5. S. P. Ranganadham, Ind. Jour. Phys., *7*, 353 (1932).

6. A. Rousset, Thesis presented to the University of Paris (1935).

7. P. Peyrot, Comptes Rendus, *203*, 1512 (1936).

8. C. Dakshinamurti, Proc. Ind. Acad. Sci., *5*, 385 (1937).

scattered light passes through a suitably oriented double image prism and nicol and measurements are made visually by the Cornu method. The observation bulb or the outer bath may be painted black on all sides, leaving two suitable windows for incident light and scattered light respectively.

For purposes of measuring the relative scattering powers of liquids, a nearly parallel beam, emerging from a long focus lens, is first allowed to pass through a block of homogeneous and colourless jena glass 2 cm. thick, which is chosen as a secondary standard.[1] The liquid under examination, contained in a bulb, is placed close to the block of glass and the whole system immersed in a rectangular bath containing a suitable liquid. Windows for the entry of the incident light and the exit of the scattered light are provided and the rest painted black. The apertures, through which the scattered light comes out, are small rectangles adjacent to each other and situated on either side of the surface of contact between the liquid bulb and the standard glass. An opaque portion of about 4 mm. separates the two apertures and serves to cut off the light diffused at the surface of contact. The comparison is made with the help of an Abney rotating sector photometer. The secondary standard is finally compared with a freshly prepared bulb of ethyl ether, the intensity of the scattered light from which is taken as unity.

Sweitzer[2] has developed a more elaborate method in which the scattered light is compared with the light from the source itself. Fig. 16 shows the disposition of this apparatus. Light from A, the positive crater of a carbon arc, is rendered parallel with the help of a lens L. The parallel beam is further limited by a system of apertures. It partly gets into the container C and is partly reflected by a glass plate R to M′ and then to M″ and M‴. After passing through a blue glass N, it reaches a Lummer cube E. The scattered light reaches the Lummer cube directly. The two beams are matched against each other with the help of a wedge W introduced in the path of the direct

[1] The choice of the secondary standard is somewhat arbitrary.

[2] Jour. Phys. Chem., *31*, 1150 (1927).

light. The function of N is to secure a bluish tinge to the direct light so that its colour may resemble that of the scattered light, enabling a proper match to be effected. A filter Q of quinine sulphate is inserted in the path of the incident light so as to cut off the radiations of wave-lengths smaller than about $\lambda 4000$.

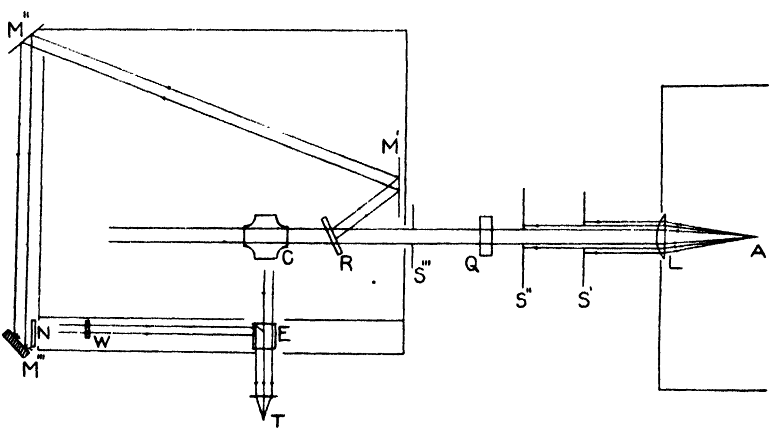


FIG. 16.

The experimental technique adopted for measuring the absolute scattering power is similar to that adopted in the case of gases. Cabannes and Daure compared the light scattered by liquid benzene with that scattered by ethyl chloride gas using the same bulb as has been used by Daure for ethyl chloride gas (Fig. 14) and thus obtained the absolute scattering power of liquid benzene.

Effect of Temperature, Pressure, etc., on the Character of the Scattered Light.—It has already been pointed out that formulae 15*a* and 16 of chapter V, for the depolarization and intensity of the scattered light respectively, in dense media, are of wide applicability. In their derivation, no special assumptions have been made regarding the state of aggregation in the medium except that the fluctuations in density are given by the Einstein-Smoluchowski expression. Extensive data have been obtained, notably by Raman and his collaborators, with different

substances over a wide range of physical states and conditions. Ramanathan[1] studied the scattering in saturated ether vapour and the liquid itself in the temperature range 30° to 190°C. and also in the gaseous phase above the critical temperature. Subsequently, Raman and Ramanathan[2] studied the scattering of light in carbon dioxide gas in: (i) unsaturated vapour, (ii) saturated vapour in thermal equilibrium with the liquid, (iii) liquid under the pressure of its own vapour, (iv) liquid under impressed pressure higher than the vapour pressure, (v) substance in the vicinity of the critical state, and (vi) substance in the gaseous state above the critical temperature. The apparatus used by them has already been described (Fig. 8). The more recent work of Ramachandra Rao on the intensity of the light scattered by liquids at different temperatures has also been described in an earlier section. The main results implied in equation (16) of chapter V and verified experimentally by the foregoing authors are:—

(i) the intensity of scattering is given by formula (16) of chapter V over a wide range of physical states, except in the vicinity of the critical temperature,

(ii) the intensity of scattering increases rapidly as the critical point is approached,

(iii) the scattering powers of the saturated vapour, liquid and gaseous phases approach each other and converge to a very large value at the critical point, and

(iv) the depolarization of the scattered light decreases with increasing temperature or increasing pressure and becomes vanishingly small at the critical state.

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[1] Proc. Roy. Soc., *102*, 151 (1922).

[2] *Ibid.*, *104*, 357 (1924).

CHAPTER VII

BINARY LIQUID MIXTURES AND LIQUID BOUNDARIES

Introduction.—We have seen that in the case of a dense medium composed of one kind of molecules only, random fluctuations in the physical properties of the individual volume elements may occur on account of two causes. These have been designated respectively as fluctuations in number and fluctuations in orientation. We accordingly get two kinds of scattering, namely, the density scattering and the anisotropic scattering, due respectively to the former and the latter types of fluctuation. In the case of a binary liquid mixture, a given volume element at a given instant may differ from another not merely in possessing a different density and a different arrangement in space of the anisotropic molecules but also in having a different concentration. Chance fluctuations of concentration are bound to occur and as a consequence, a third type of scattering will arise and this may be called concentration scattering. The total scattering I, in such a case, will consist of three parts as shown in (1).

$$I = I_c + I_a + I_d \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

I_c is the concentration scattering and does not exist in media composed of one kind of molecules only. I_a is the anisotropic scattering and does not exist if the medium is composed of spherical molecules only. I_d is common to all matter. We shall now evaluate I in the general case of a binary liquid mixture.

Polarized Scattering from a Binary Liquid Mixture.—The whole medium may, as before, be divided into small volume elements, the volume of each of which is V. The average intensity of the light scattered by each volume element of such a medium in a transverse direction, when expressed as a fraction of the incident energy for unpolarized incident light, is (see 2*a* of chapter V)

$$\frac{\pi^2 V^2}{2\lambda^4 r^2}\overline{(\Delta\varepsilon)^2}. \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

Substituting for $\overline{(\triangle\varepsilon)^2}$ in (2) from (20) of Appendix III, we obtain (3) for the intensity of the scattered light per unit volume of the medium.[1]

$$\frac{\pi^2 RT}{2N\lambda^4 r^2}\left[\left(\frac{\partial\varepsilon}{\partial c}\right)^2 \Big/ m_1\left(v_2\frac{\partial p_2}{\partial c} - S_2\frac{\partial\varphi}{\partial c}\right) + \beta\sigma^2\left(\frac{\partial\varepsilon}{\partial\sigma}\right)^2\right]. \qquad (3)$$

The first term in (3) represents the light scattering due to fluctuations of concentration in the mixture (I_c). The second term represents the light scattering due to fluctuations of density when the mixture is regarded as a single liquid (I_d). Both these effects give rise to scattered light which is linearly polarized, when observations are made in a transverse direction, irrespective of whether incident polarized or unpolarized light is used. In other directions, the laws of intensity and polarization are exactly the same as those that have been derived for pure density scattering. After substitution from (4) of chapter V, the second term of (3) may easily be seen to reduce to (6) of chapter V, as it ought to. The first term (I_c) may be further simplified, if we neglect $S_2\frac{\partial\varphi}{\partial c}$ in comparison with $v_2\frac{\partial p_2}{\partial c}$ and assume that the saturated vapour obeys the gas laws. It may then be written as

$$\frac{\pi^2 M_2}{2N\lambda^4 r^2}\cdot\frac{\frac{1}{m_1}\left(\frac{\partial\varepsilon}{\partial c}\right)^2}{\frac{\partial \log p_2}{\partial c}} \qquad (4)$$

M_2 is the molecular weight of the second component in the gaseous phase. This result, originally obtained by Einstein,[2] refers to the concentration scattering under certain simplifying assumptions. The simplifications made are only permissible when the total vapour pressure is not large.

The relative importance of the two effects, namely, the light scattering due to fluctuations of density and of concentration respectively, depends on the circumstances of the particular

[1] The significance of the various letters and symbols occurring in this section is explained in Appendix III.

[2] Ann. d. Phys., *33*, 1275 (1910).

case. In the immediate neighbourhood of the critical solution temperature, the partial vapour pressures alter very little with the composition of the mixture and the concentration scattering is easily seen to become very great. This accounts for the well-known phenomenon of critical opalescence. On the other hand, at temperatures far removed from the critical solution point or in cases in which the components are ordinarily completely miscible, the partial vapour pressures change rapidly with concentration and the concentration scattering becomes very small. The density scattering is, however, an inherent property of the medium and is governed by the usual factors. It is evident that when either of the components forms only a small proportion of the mixture (very dilute solutions), the concentration scattering would disappear and the observed result would be due entirely to the density scattering.

Anisotropic Scattering.—The anisotropic scattering (I_a) may be evaluated directly in terms of the constants appropriate to the individual molecules as has been done in the case of a pure liquid. As the treatment is quite similar and formal, it need not be repeated here. It is, however, more useful to express this in terms of the polarized scattering and the observed depolarization of the scattered light. If ϱ is the depolarization factor, it is easily shown that the total intensity of the scattered light is given by (5).

$$(I_c+I_d)\left(\frac{6+6\varrho}{6-7\varrho}\right) \quad \ldots \quad \ldots \quad \ldots \qquad (5)$$

I_c+I_d stands for the aggregate polarized scattering.

Aggregate Intensity.—Thus the complete expression for the intensity of the light scattered per unit volume of a binary liquid mixture of concentration c, in a transverse direction, when incident unpolarized light of intensity I_0 is used, is given by (6).

$$\frac{I}{I_0} = \frac{\pi^2 RT}{2N\lambda^4 r^2}\left[\left(\frac{\partial \varepsilon}{\partial c}\right)^2 \Big/ m_1\left(v_2\frac{\partial p_2}{\partial c} - S_2\frac{\partial \varphi}{\partial c}\right) + \beta\sigma^2\left(\frac{\partial \varepsilon}{\partial \sigma}\right)^2\right]\left(\frac{6+6\varrho}{6-7\varrho}\right) \quad \ldots \qquad (6)$$

ϱ stands for the observed depolarization of the light scattered by the mixture in question, in a transverse direction. In the

derivation of this anisotropic factor, use is made of the fact that the anisotropic scattering is depolarized and has a depolarization factor 6/7 in the transverse direction, when unpolarized incident light is used.

In the expression (6), $\frac{\partial p_2}{\partial c}$ and $\frac{\partial \varphi}{\partial c}$ are readily calculated from experimental data, if the vapour pressures at different concentrations are available for the given mixture. $\frac{\partial \varepsilon}{\partial \sigma}$ and $\frac{\partial \varepsilon}{\partial c}$ have to be obtained in the following manner. As before, we may either use the Clausius-Mosotti law $\frac{\varepsilon-1}{\varepsilon+2} = \sigma \times \text{constant}$ or its modified form $\varepsilon-1 = \sigma \times \text{constant}$ and obtain alternative values for $\frac{\partial \varepsilon}{\partial \sigma}$. For reasons already explained, the latter is the more appropriate form, when we are dealing with small volume elements and has accordingly to be used. This gives $\frac{\partial \varepsilon}{\partial \sigma} = \frac{\varepsilon-1}{\sigma}$. The dielectric constant ε of the mixture of a certain concentration may be expressed as

$$\varepsilon-1 = (\beta_1 m_1 + \beta_2 m_2)\frac{\varepsilon+2}{3}$$

where β_1 and β_2 are constants characteristic of each one of the constituents respectively. According as we regard $\varepsilon+2$, on the right hand side, as a constant or as a variable, we obtain respectively

$$\frac{\partial \varepsilon}{\partial c} = \frac{\varepsilon+2}{3} \cdot \frac{\partial(\beta_1 m_1 + \beta_2 m_2)}{\partial c}$$

or $$\left(\frac{\partial \varepsilon}{\partial c}\right)_0 = \left(\frac{\varepsilon+2}{3}\right)^2 \frac{\partial(\beta_1 m_1 + \beta_2 m_2)}{\partial c}.$$

The former is the appropriate value when we are dealing with small volume elements but the latter applies to the medium as a whole. By plotting the observed dielectric constant against the concentration, we can obtain $\left(\frac{\partial \varepsilon}{\partial c}\right)_0$ at any desired

concentration and dividing the result by $\frac{\varepsilon+2}{3}$, we get the value of $\frac{\partial \varepsilon}{\partial c}$ which should be used in expression (6). Thus, all the quantities occurring in (6) are either calculable or may be directly determined by experiment. It may finally be noted that if it is required to verify the theory in the case of a binary liquid mixture, it is necessary to have a knowledge of its dielectric constant and its variation with concentration, its density, refractive index, depolarization of the scattered light, isothermal compressibility, temperature, partial and total vapour pressures and their variation with concentration, specific volumes of the vapours and the shrinkages in volume produced on dissolving a known quantity of the solute in the solvent. All these data are available only in one or two cases and accordingly we should regard the experimental work so far done in this direction as very meagre.

Experimental Results.—On account of the various parameters involved in the expression for the intensity of the light scattered by a binary liquid mixture, the collection of complete data in respect of several mixtures becomes somewhat elaborate. Some of the main results only will be mentioned here. Expression (4) has been verified by Zernicke[1] in the case of a number of liquid mixtures in the neighbourhood of their critical solution temperatures. Quantitative measurements have been made by Fürth,[2] Martin and Lehrman,[3] Rav,[4] Parthasarathy[5] and several others. The general features of (6) are verified in all the cases. Mention may be made of the following facts. In completely miscible liquids and at temperatures far from the critical solution temperatures in the case of partially miscible liquids, the concentration scattering is either altogether negligible or very small in comparison with the density scattering. Near the critical solution temperatures, the concentration scattering becomes

[1] Thesis, Amsterdam (1914).
[2] Wien Berichte, *124*, 577 (1915).
[3] Jour. Phys. Chem., *26*, 75 (1922).
[4] Proc. Ind. Assoc. Cult. Sci., *9*, 19 (1925).
[5] Ind. Jour. Phys., *8*, 275 (1933).

very large in comparison with other types of scattering. The orientation scattering, which contributes to the depolarization, increases only in proportion to the density and the depolarization of the aggregate scattering accordingly diminishes rapidly as we approach the critical solution temperature.

Scattering of Light by Liquid Boundaries.—The scattering phenomena, which have hitherto been dealt with, are characteristic only of transparent media and may all be described by one common name, *the internal or body opalescence*. Smoluchowski [1] first suggested that under certain special circumstances such as in the vicinity of the critical state, a substance may exhibit a different and distinctive phenomenon, which may be called *the surface opalescence*. Long after the suggestion of Smoluchowski, Mandelstam [2] made some observations by allowing light to fall on the boundary between two layers of a mixture of carbon disulphide and methyl alcohol near their critical solution temperature. As a result of these studies, Mandelstam concluded that in directions not far removed from that of regular reflection, there was also some scattered light and expressed the opinion that the effect was analogous to that predicted by Smoluchowski for the critical state of a single liquid. More recently, Raman and Ramdas [3] examined the problem of the scattering of light by liquid boundaries, for various angles of incidence under a wide range of physical conditions, in about sixty liquids.

The case of clean mercury, which is of special interest, has been investigated by them in great detail and may be dealt with here as a separate entity. In the case of normal incidence of unpolarized light, the direction of incidence being vertically downwards, the following observations have been made. No striking variations of intensity are observed as the direction of observation is gradually altered from the vertical to the horizontal. When viewed nearly vertically, the scattered light exhibits no polarization but as the line of observation is more

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[1] Ann. d. Phys., *25*, 228 (1908).
[2] *Ibid.*, *41*, 609 (1913).
[3] Proc. Roy. Soc., *108*, 561 (1925); *109*, 150 and 272 (1926).

and more inclined towards the horizontal, marked polarization sets in. The light scattered in a grazing direction is almost completely polarized, *the principal component of the electric vector being then perpendicular to the surface.* It may be noted that in this respect the result is totally different from that encountered in ordinary Rayleigh scattering. In the case of normal incidence of plane polarized light, the phenomena observed are satisfactorily represented by Fig. 17. The lengths of the arrows give an idea of the intensity and the directions indicate the direction of the principal vibration in the scattered light.

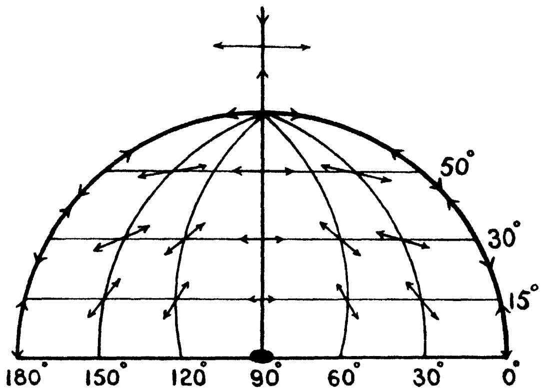


FIG. 17.

The intensity as well as the state of polarization vary greatly with the azimuth of observation. Scattered light is of greatest intensity in the azimuth containing the electric vector of the incident waves and is polarized in such a manner that the principal component of the electric vector is parallel to the direction of incidence. It has a minimum intensity in azimuths perpendicular to the above. Cases, where light is incident at other angles, have also been studied by these authors. By adopting intermediate standards, they arrived at the result that the light scattered by a clean mercury surface, illuminated normally with unpolarized light in the green part of the solar spectrum and viewed at 45°, has an intensity which is only $0{\cdot}57\times10^{-6}$ times the brightness of a surface of plaster of paris

when viewed under the same conditions. The corresponding figure for transparent liquids is about 50 to 100 times larger. The case of ether, in which it is $43 \cdot 4 \times 10^{-6}$, may be cited for comparison. Besides mercury, Raman and Ramdas have studied a large number of transparent liquids and Table XII gives the results obtained by them in some typical cases.

The notable features of these results are given below. The lighter paraffins, which have a low surface tension, exhibit a conspicuous surface scattering. Formic acid, while showing practically the same internal scattering as acetic, propionic and butyric acids, exhibits a much smaller surface scattering than the others. This result may be connected with the high surface tension of formic acid in comparison with that of its higher homologues. Water, which has a high surface tension, has a low surface scattering, lower than that found in any other liquid except mercury. The transparent liquids show a surface scattering which is about 50 to 100 times more intense than that observed with mercury. The surface tension of mercury is, on the other hand, about 20 to 30 times larger than that of the transparent liquids. These results clearly show that the phenomenon of surface scattering has a genuine molecular origin and that it is closely connected with the state of tension to which the molecules in the surface are subjected. We may expect that the greater the surface tension, the more closely would the surface, under thermal agitation, approximate to a perfect optical plane and the smaller would be the surface scattering. The fact, that such an expectation is fully justified by the observations given in the accompanying Table, permits us to conclude that the surface scattering has its origin in the thermal fluctuations to which the oriented molecules at the surface are subjected. Such a fluctuation scattering would therefore increase with increasing temperature and decrease with increasing surface tension.

Raman and Ramdas have also studied the effect of contamination and of approach to critical temperature on the phenomenon and also the changes produced when the surface is one of separation between two liquids, instead of between a liquid and its own vapour. An intimate connection is thus established between the intensity of surface scattering and the nature of the

TABLE XII

Intensity of Surface Scattering in Liquids : Surface of Water as Standard

Substance	Surface tension	Intensity of surface scattering (water = 1)	Intensity of body scattering (water = 1)
Water	72	1	1
Pentane	..	11·3	5·7
Isopentane	14	8·9	5·3
Hexane	16	8·5	5·9
Heptane	..	8·8	5·9
Octane	20	7·8	4·8
β-iso-amylene	..	10·8	7·7
Ethylene chloride ..	30	3·8	8·5
Chloroform	25	6·3	7·4
Carbon tetrachloride ..	25	12·6	6·0
Silicon ,, ..	16	7·4	..
Formic acid	36	4·6	6·1
Acetic acid	24	4·9	5·6
Propionic acid ..	27	5·8	6·2
Butyric ,, ..	27	6·3	6·0
Ethyl ether	15	7·4	5·9
Methyl alcohol ..	23	4·0	2·7
Ethyl ,, ..	22	5·2	3·2
Isopropyl ,, ...	21	7·2	3·1
Butyl ,, ..	24	7·4	3·5
Isobutyl ,, ..	23	9·3	3·7
Trimethyl carbinol ..	..	6·6	3·5
Albyl alcohol ..	23	7·8	6·1
Benzyl ,, ..	40	10·0	12·4
Ethyl formate ..	22	5·2	5·0
Propyl ,, ..	22	7·4	4·7
Propyl acetate ..	22	5·6	4·8
Acetaldehyde ..	..	4·9	4·5
Methyl ethyl ketone ..	..	5·3	4·0
Mercury	547	0·1	..

surface and the extent of tension under which the molecules in it are.

Chapter VIII

OPTICAL ANISOTROPY AND MOLECULAR STRUCTURE

Relation of Depolarization to the Optical Anisotropy of Molecules in the Liquid and Vapour States.—Equations (2) of chapter IV and (15) of chapter V express the relationship between $\varrho_{vap.}$, $\delta_{vap.}$ and $\varrho_{liq.}$, $\delta_{liq.}$ respectively. $\delta_{liq.}$ and $\delta_{vap.}$, calculated for a number of substances from the observed values of $\varrho_{liq.}$ and $\varrho_{vap.}$, are collected here from Tables II and XI for comparison.

Table XIII

Optical Anisotropy in the Liquid and Vapour States

Substance	$\delta_{liq.} \times 10^3$	$\delta_{vap.} \times 10^3$	Substance	$\delta_{liq.} \times 10^3$	$\delta_{vap.} \times 10^3$
Water	4·9	17·1	Diethyl ether ..	3·7	21·5
Carbon disulphide ..	72·4	110·7	Ethyl acetate ..	8·2	18·8
Carbon tetrachloride ..	1·6	1·7	Amyl alcohol ..	1·5	11·0
Chloroform ..	9·3	15·3	Hexane	2·8	12·7
Methyl alcohol ..	3·5	14·5	Benzene	18·9	39·6
Ethylene chloride ..	14·0	29·5	Chlorobenzene ..	30·6	43·3
Ethyl bromide ..	13·9	19·7	Aniline	21·6	54·7
Ethyl alcohol ..	2·6	7·6	Nitrobenzene ..	35·8	54·7
Acetic acid ..	25·1	25·9	Heptane	2·1	13·6
Propyl alcohol ..	1·9	10·1	Toluene	20·4	37·7
Isopropyl alcohol ..	1·1	11·0	Metaxylene.. ..	18·8	44·2
Acetone	12·7	13·6	Butyl alcohol ..	1·6	14·5

$\delta_{liq.}$ and $\delta_{vap.}$ should really have been identical with each other[1] if the polarization field in liquids is of the Lorentz-Lorenz type, contributing $\frac{4\pi\chi E}{3}$ in all directions to the incident field E. The fact that they are so widely different from each other in a large number of cases ($\delta_{liq.}$ being usually smaller than $\delta_{vap.}$) is one of the most significant experimental facts and has

[1] This follows easily if we combine equations (15) and (18) of chapter V with (2) of chapter IV.

TABLE XIV

Dependence of the Effective Optical Anisotropy in the Liquid State on Temperature : $\delta \times 10^3$

Substance. \ Temperature °C.	30	40	50	60	70	80	90	100	110	120	130	140	150	160	170	Vapour
Methyl alcohol ..	4·3	4·7	5·1	5·6	6·2	6·8	7·3	8·0	8·2	8·5	8·7	9·0	9·2	9·9	11·1	14·5
Ethyl ,, ..	2·5	2·8	3·0	3·2	3·4	3·5	3·7	3·8	3·9	3·7	3·9	3·7	3·9	4·3	5·2	7·6
Propyl ,, ..	2·2	2·4	..	2·7	..	2·9	..	2·9	..	3·0	..	3·3	..	3·8	..	10·1
Butyl ,, ..	2·1	2·3	2·4	2·5	2·6	2·7	2·7	2·7	2·6	2·8	..	..	..	..	..	14·5
Acetic acid ..	34·4	34·1	..	32·3	..	24·2	..	20·7	..	19·2	..	20·8	..	21·1	..	25·9
Propionic ,, ..	19·4	20·2	21·0	21·4	20·2	17·0	17·0	17·6	..	18·7	..	20·2	..	20·5	..	23·2
Butyric ,, ..	9·3	9·4	9·1	9·3	9·9	10·0	11·3	11·6	..	13·6	..	13·1	..	12·7	..	17·1
Benzene	22·1	23·8	..	28·1	..	32·6	..	34·6	..	36·1	..	37·7	..	38·0	..	39·6
Nitrobenzene ..	36·8	37·0	35·1	31·2	26·1	21·2	16·2	14·8	..	..	..	..	..	..	..	54·7
Aniline	21·4	21·3	..	20·2	..	17·1	..	15·0	..	14·0	..	13·4	..	13·7	..	54·7
Bromobenzene ..	29·9	30·5	..	33·4	..	35·4	..	36·2	..	40·9	..	41·1	..	41·6	..	47·1
Ethylbenzene ..	18·4	19·6	20·8	21·7	23·0	24·4	25·9	27·3	..	30·1	..	32·5	..	..	..	41·4

been the starting point of the theory of the anisotropic optical polarization field originated by Raman and Krishnan and briefly described in an earlier chapter.

The gradual passage of the effective anisotropy exhibited in the liquid phase to that observed in the corresponding vapour has been followed by Krishnan[1] and later by Ramachandra Rao[2] in a few liquids. The data obtained by Ramachandra Rao are given here for purposes of illustration.

General Considerations.—The figures given in Table II show very convincingly that practically all the molecules are optically anisotropic. The values of the depolarization factors in individual cases give a rough idea of the order in which the molecules have to be placed with regard to their optical anisotropy. The most significant facts are the zero values of ϱ assigned to argon and methane, the very small value for CCl_4 vapour, and the comparatively large values for molecules like CO_2, CS_2, etc. This at once suggests that symmetry of structure plays an important part in determining the shape or the eccentricity of the polarizability ellipsoid. The theories put forward by Lord Rayleigh and Born for the explanation of the imperfection of polarization of scattered light start from the assumption that molecules, in general, are optically anisotropic. It is, however, obviously of utmost importance to seek for the origin of such optical anisotropy in molecules in order to obtain a quantitative estimate of the same from their known structures. The earliest attempts in this direction were those of Silberstein.[3] These attempts were based on the idea of a mutual interaction between the various induced doublets in a molecule. Proceeding on somewhat similar lines, Bragg[4] successfully explained the double refraction exhibited by calcite and aragonite crystals. Following a suggestion by Raman,[5] Ramanathan[6] proceeded to examine how far these ideas could be applied for calculating quantitatively

[1] Proc. Ind. Assoc. Cult. Sci., *9*, 251 (1926).
[2] Ind. Jour. Phys., *2*, 7 (1927) and *3*, 1 and 21 (1928).
[3] Phil. Mag., *33*, 92, 215 and 521 (1917).
[4] Proc. Roy. Soc., *105*, 370 (1924).
[5] Nature, *114*, 49 (1924).
[6] Proc. Roy. Soc., *107*, 684 (1924).

the optical anisotropy of certain simple molecules possessing well-known configurations. The ideas underlying the investigation of the above authors are as follows. Every atom in a molecule is polarized under the action of the incident light wave. So far as its external field is concerned, it may be replaced by an electric doublet of the requisite strength situated at its *optical centre.* If the atoms in a molecule are so far removed from one another that the field created by the doublet of any one atom at any other is negligible, then the effective field acting at each atom will be practically identical with the actual field. The polarizability of the molecule as a whole will merely be the sum of the polarizabilities of the various atoms irrespective of the direction of the incident electric vector. In practice, however, owing to the close proximity of the constituent atoms in a molecule, the doublet of each atom creates a field around itself according to the usual laws of electrostatics and thus enhances or diminishes as the case may be, to different extents in different directions, the field acting on its neighbours. The result is that the aggregate polarizability of the molecule is enhanced in certain directions and diminished in certain other directions and the molecule acquires optical anisotropy. We shall now consider certain simple cases individually.

Diatomic Molecules.—If we consider a diatomic molecule, say XX, and if the moment induced by an electric vector E acting in the direction of the line of centres is EC, composed of $\frac{EC}{2}$ from one X and $\frac{EC}{2}$ from the other, we may write down the equation

$$\frac{EC}{2} = E'\alpha_0 = \left(E + \frac{EC}{r^3}\right)\alpha_0.$$

α_0 is the polarizability of each atom in an isolated condition. The field E′ acting on each atom consists of a term $\frac{2}{r^3} \cdot \frac{EC}{2}$, arising from a doublet strength $\frac{EC}{2}$ at the other, which is at a distance r, besides the original field E. Similarly we have

$$\frac{EA}{2} = E'\alpha_0 = \left(E - \frac{EA}{2r^3}\right)\alpha_0,$$

where EA is the moment induced in the molecule when the electric vector E is acting in a direction normal to the line of centres. C and A, the principal polarizabilities of the molecule, may now be expressed as

$$C = \frac{2\alpha_0}{1 - \frac{2\alpha_0}{r^3}}; \quad A = \frac{2\alpha_0}{1 + \frac{\alpha_0}{r^3}} \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

The average polarizability α of the molecule is given by (2).

$$\alpha = \frac{C+2A}{3} = \frac{2\alpha_0}{3}\left\{\frac{1}{1 - \frac{2\alpha_0}{r^3}} + \frac{2}{1+\frac{\alpha_0}{r^3}}\right\}. \quad \ldots \quad (2)$$

This reduces to $2\alpha_0$ when $r = \infty$, which means that the polarizability of a molecule is merely the sum of the polarizabilities of the constituent atoms when they are at such large distances that the terms arising from mutual action between the induced doublets are negligible. Otherwise, the polarizability is always *more in the direction of the line of centres* and *less in directions perpendicular thereto*. The average is slightly more than what would have been obtained on the law of additivity.

Similar reasoning may be applied in the case of a molecule of the type XY. If out of the total moment EC, induced by an electric vector E acting along the line of centres, EC_x is from X and EC_y is from Y, we have

$$EC_x = \alpha_1\left(E + \frac{2EC_y}{r^3}\right)$$

$$EC_y = \alpha_2\left(E + \frac{2EC_x}{r^3}\right).$$

α_1 and α_2 are the polarizabilities of the X and Y atoms respectively. In a perpendicular direction, we have for EA_x and EA_y which make up EA,

$$EA_x = \alpha_1\left(E - \frac{EA_y}{r^3}\right),$$

$$EA_y = \alpha_2\left(E - \frac{EA_x}{r^3}\right).$$

On solving the equations, we obtain the following expressions for C and A, the principal polarizabilities of the molecule.

$$\left.\begin{aligned} \mathrm{C} = \mathrm{C}_x+\mathrm{C}_y &= \frac{\alpha_1+\alpha_2+4\alpha_1\alpha_2/r^3}{1-4\alpha_1\alpha_2/r^6} \\ \mathrm{A} = \mathrm{A}_x+\mathrm{A}_y &= \frac{\alpha_1+\alpha_2-2\alpha_1\alpha_2/r^3}{1-\alpha_1\alpha_2/r^6} \end{aligned}\right\} \quad \ldots \quad \ldots \quad (1a)$$

These equations naturally reduce to (1) if we put $\alpha_1 = \alpha_2 = \alpha_0$. The average polarizability of the molecule is again given by $\frac{\mathrm{C}+2\mathrm{A}}{3}$.

Polyatomic Molecules.—Following the same reasoning, Havelock[1] has shown that for a molecule of the type YX_2, in which the angle between the two YX lines is 2β, the principal polarizabilities are given by

$$\mathrm{A} = \frac{2\alpha_1+\alpha_2+\frac{\alpha_1\alpha_2}{r^3}\left(\frac{1}{8\sin^3\beta}-4\right)}{1+\frac{\alpha_1}{8r^3\sin^3\beta}-\frac{2\alpha_1\alpha_2}{r^6}}$$

$$\mathrm{B} = \frac{\left(1+\frac{\alpha_1}{4r^3\sin^3\beta}\right)\left\{2\alpha_1+\alpha_2+\frac{\alpha_1\alpha_2}{r^3}\left(\frac{1}{8\sin^3\beta}-4+12\cos^2\beta\right)\right\}-36\frac{\alpha_1{}^2\alpha_2}{r^6}\sin^2\beta\cos^2\beta}{\left(1+\frac{\alpha_1}{4r^3\sin^3\beta}\right)\left\{1+\frac{\alpha_1}{8r^3\sin^3\beta}-\frac{2\alpha_1\alpha_2}{r^6}(1-3\cos^2\beta)^2\right\}-18\frac{\alpha_1\alpha_2}{r^6}\left(1+\frac{\alpha_1}{8r^3\sin^3\beta}\right)\sin^2\beta\cos^2\beta}$$

$$\mathrm{C} = \frac{\left(1-\frac{\alpha_1}{8r^3\sin^3\beta}\right)\left\{2\alpha_1+\alpha_2-\frac{\alpha_1\alpha_2}{r^3}\left(\frac{1}{4\sin^3\beta}+4-12\sin^2\beta\right)\right\}-36\frac{\alpha_1{}^2\alpha_2}{r^6}\sin^2\beta\cos^2\beta}{\left(1-\frac{\alpha_1}{8r^3\sin^3\beta}\right)\left\{1-\frac{\alpha_1}{4r^3\sin^3\beta}-\frac{2\alpha_1\alpha_2}{r^6}(1-3\sin^2\beta)^2\right\}-18\frac{\alpha_1\alpha_2}{r^6}\left(1-\frac{\alpha_1}{4r^3\sin^3\beta}\right)\sin^2\beta\cos^2\beta}$$

(3)

α_1 and α_2 are respectively the polarizabilities of X and Y atoms and r stands for the distance YX. If 2β is put equal to 180°, equations (3) reduce to (3*a*).

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[1] Phil. Mag., *3*, 158 and 433 (1927).

$$A = B = \frac{2\alpha_1 + \alpha_2 - \dfrac{31\alpha_1\alpha_2}{8r^3}}{1 - \dfrac{2\alpha_1\alpha_2}{r^6} + \dfrac{\alpha_1}{8r^3}}$$

$$C = \frac{2\alpha_1 + \alpha_2 + \dfrac{31\alpha_1\alpha_2}{4r^3}}{1 - \dfrac{8\alpha_1\alpha_2}{r^6} - \dfrac{\alpha_1}{4r^3}}. \quad \ldots \quad \ldots \quad (3a)$$

These expressions are appropriate to linear triatomic molecules of the type of CO_2 and CS_2. They may also be derived independently as has been done by Ramanathan[1].

If 2β is put equal to 60° and $\alpha_1 = \alpha_2 = \alpha_0$, equations (3) reduce to (3*b*) on simplification.

$$A = \frac{3\alpha_0}{1 + \dfrac{2\alpha_0}{r^3}}$$

$$B = C = \frac{3\alpha_0\left(1 + \dfrac{\alpha_0}{2r^3}\right)}{1 - \dfrac{\alpha_0}{2r^3} - \dfrac{11\alpha_0^2}{4r^6}}. \quad \ldots \quad \ldots \quad (3b)$$

These expressions are appropriate to a molecule of the type X_3 having an equilateral configuration with the side equal to r. Havelock and Cabannes have extended these methods to some more complicated structures such as those possessing a tetrahedral symmetry, etc.

Comparison with Experiment.—From (1) it will be noticed that

$$\frac{C}{A} = \frac{1 + \alpha_0/r^3}{1 - 2\alpha_0/r^3}. \quad \ldots \quad \ldots \quad \ldots \quad (4)$$

Since the depolarization factor for a diatomic molecule is given by (see 19 of chapter III)

$$\varrho = \frac{2(C-A)^2}{9A^2 + 4C^2 + 2AC},$$

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[1] Proc. Roy. Soc., *107*, 684 (1924).

we can obtain a value for $\frac{C}{A}$ from the observed value of ρ. If this is substituted in (4), we obtain α_0/r^3. From the known refractive index n of a gas, which is connected with the principal moments C and A and the average polarizability α by the relation

$$\frac{n^2-1}{4\pi} = \nu \cdot \frac{C+2A}{3} = \nu\alpha ,$$

we obtain a value for $\frac{C+2A}{3}$. If the values of $\frac{C+2A}{3}$ and α_0/r^3 so derived are substituted in (2), we get α_0 and hence r^3 also. This gives the distance between the *optical centres*. In the following Table, the values so calculated for four diatomic molecules are compared with the inter-nuclear distances derived from two other sources.

TABLE XV

Optical Anisotropy and Nuclear Distances

Gas	$(n^2-1)\times 10^4$ for λ4860.	ρ	$(C+2A)\times 10^{24}$	$\frac{C}{A}$	$\alpha_0\times 10^{24}$	$r\times 10^8$	$r\times 10^8$ (band spectra)	$r\times 10^8$ (viscosity)
H_2 ..	2·812	0·027	2·486	1·541	0·3976	1·44	0·75	1·36
O_2 ..	5·470	0·065	4·837	1·958	0·7300	1·55	1·20	1·81
N_2 ..	6·024	0·036	5·326	1·644	0·8407	1·78	1·22	1·89
Cl_2 ..	15·380	0·041	13·590	1·700	2·1280	2·37	1·98	2·70

The general agreement, particularly in the order of magnitude, between the values obtained from the data on light scattering and the values obtained by other methods is very satisfactory. It may, however, be noted that the values obtained from light scattering are invariably greater than those obtained from band spectra. This may be expected, as the centres of the electrical doublets which have been called the *optical centres* will not, in general, coincide with the positions of the nuclei but will be determined more by the distribution of the electron density in the molecule. In the case of polyatomic molecules also, similar calculations have been made by Ramanathan and by Cabannes and good agreement is obtained in respect of the order of magnitude. In spite of the apparent success of the

above theory, it is well to remark here that it is only of a very limited and qualitative nature and the drawbacks of the same will become even more obvious when we come to consider its extension to the theory of Raman scattering.

General Relationships between Molecular Structure and Optical Anisotropy.—The figures given in Table II permit us to draw the following conclusions:

(1) Aromatic and unsaturated ring compounds are usually more anisotropic than the aliphatic or the saturated ring compounds. This is evident on comparing benzene with cyclohexane or hexane.

(2) Amongst the aliphatic compounds themselves, increasing unsaturation produces increasing optical anisotropy. This is evident on comparing the series ethane, ethylene and acetylene.

(3) Homonuclear molecules are usually more anisotropic than the heteronuclear ones. This is evident on comparing H_2, N_2, O_2 on the one hand with HCl, NO, CO, etc., on the other.

(4) Atoms and molecules, in which the atoms are symmetrically disposed, exhibit a very small or no optical anisotropy. The cases of argon, methane and carbon tetrachloride are examples. Exceptions in SiF_4 and $SiCl_4$ may be noted.

CHAPTER IX

OPTICAL ANISOTROPY AND DIFFERENT TYPES OF BIREFRINGENCE

Natural Birefringence.—The earliest attempts to explain the natural birefringence exhibited by crystals, by postulating certain structures, were those of Ewald. About the same time, a very comprehensive treatment in respect of the physical properties of crystals was published by Born[1] and many attempts were then made to apply his methods for calculating the optical constants of certain crystals such as Hg_2Cl_2, etc. The calculations involved are somewhat complicated and cannot easily be extended to other cases. Bragg[2] has attacked the problem from a different point of view and successfully applied his methods to the case of several carbonates. The general principles underlying this method have already been indicated in the previous chapter in connection with the anisotropy of molecules. We shall now see how the known plane structure of the CO_3 groups in calcite crystals can satisfactorily account for the magnitude of the observed birefringence and for the fact that this crystal is optically uniaxial with its optic axis normal to the planes of the CO_3 groups.

In the foregoing chapter, it was shown that the effective refractivity of an atom, when it is surrounded by close neighbours, is different from what it would be when it is in an isolated condition. Such a difference is also, in general, dependent upon the direction in which the refractivity is being calculated. This result has the important consequence of making a molecule optically anisotropic except in the special case where the constituent atoms are symmetrically distributed within the molecule. In the case of a crystal consisting of different kinds of atoms, denoted by the subscripts 1, 2 ...... etc., we may denote their respective polarizabilities in an isolated state by α_1, α_2 .... etc.,

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[1] *Dynamik der Kristallgitter* (1915).

[2] Proc. Roy. Soc., *105*, 370 (1924).

and if their effective contributions to the refractivity in a particular direction x are given by $C_1^x\,\alpha_1$, $C_2^x\,\alpha_2$ ..... etc., we have the following equation :

$$\frac{P_x}{E}=\frac{n_x^2-1}{4\pi}=\left(1+\frac{4\pi P_x}{3E}\right)[C_1^x\alpha_1\nu_1+C_2^x\alpha_2\nu_2\ldots]. \quad (1)$$

P_x is the total optic moment induced per unit volume of the crystal when the electric vector E acts in the x direction. In (1), $E\left(1+\frac{4\pi P_x}{3E}\right)$ stands for the effective field E′, derived on the assumption that the polarizable matter is spherically symmetrically distributed. ν_1, ν_2 ... etc., represent the number of atoms of kinds 1, 2... etc., respectively that are contained in each c.c. of the crystal. Substituting for $\frac{P_x}{E}$ and slightly rearranging, we may write (1) as

$$n_x^2-1=\frac{4\pi[C_1^x\alpha_1\nu_1+C_2^x\alpha_2\nu_2\ldots\ldots]}{1-\frac{4\pi}{3}[C_1^x\alpha_1\nu_1+C_2^x\alpha_2\nu_2\ldots\ldots]} \quad \ldots \quad (2)$$

Similar equations may be obtained for the refractive index in other directions.

Equation (2) is applicable to any crystal. We shall now apply it to the case of calcite in which there are three kinds of atoms, namely, calcium (1), carbon (2) and oxygen (3). The crystal structure of calcite as revealed by X-ray analysis will now be assumed.[1] Calcium atoms are separate ions by themselves and are sufficiently far removed from the surrounding groups such that C_1 may be put equal to 1 for all directions. Taking the atomic refractivity of Ca ions from Wasastjerna [2] as 1·99, we obtain $4\pi\nu_1\alpha_1$ which is equal to $\frac{1{\cdot}99\times3\sigma}{M}$ as 0·165 if we take $\frac{M}{\sigma}$ for calcite as 36·13. The carbonate group is known to be plane and equilateral with the carbon atom at the centre and the oxygens at the corners of an equilateral triangle, the

[1] Fig. 26 given in chapter XIV shows the unit cell of calcite lattice.

[2] Soc. Scient. Fenn. Comm. Phys. Math., *1*, 37 (1923).

side of which is 2·25 A.U. We shall further assume that the carbon atom has lost all its outer electrons to the oxygens and thus contributes nothing to the refractivity, giving us $4\pi\nu_2\alpha_2 = 0$. The oxygen atoms are arranged at the corners of an equilateral triangle and such a structure will cause anisotropy of refraction. Assuming the atomic refractivity of oxygen[1] in such a combination as 3·30 and equating it to $\frac{4\pi N\alpha_3}{3}$, we obtain $\alpha_3 = 1{\cdot}30 \times 10^{-24}$. $4\pi\nu_3\alpha_3$ is merely equal to $\frac{3 \times 3{\cdot}30 \times 3\sigma}{M} = 0{\cdot}822$, as there are 3 oxygen atoms for every calcium atom in the lattice. We have already seen that for such a configuration, the effective moments per atom in directions perpendicular and parallel to the plane of the triangle (see 3*b* of chapter VIII) are given by

$$\alpha_{\perp} = \frac{\alpha_0}{1+\frac{2\alpha_0}{r^3}}, \qquad \alpha_{\parallel} = \frac{\alpha_0\left(1+\frac{\alpha_0}{2r^3}\right)}{1-\frac{\alpha_0}{2r^3}-\frac{11\alpha_0^2}{4r^6}},$$

where α_0 is the value appropriate to the isolated condition. We therefore have, in the case of calcite

$$C_3^{\perp} = \frac{1}{1+\frac{2\alpha_3}{r^3}} \quad \text{and} \quad C_3^{\parallel} = \frac{1+\frac{\alpha_3}{2r^3}}{1-\frac{\alpha_3}{2r^3}-\frac{11\alpha_3^2}{4r^6}}.$$

Substituting for α_3 and r, we obtain $C_3^{\perp} = 0{\cdot}814$ and $C_3^{\parallel} = 1{\cdot}165$. Substituting these values in turn in (2), we obtain the refractive indices for calcite when the light vector acts in a direction normal to the planes of carbonate groups and in the planes of the carbonate groups respectively. In the case of calcite, these two will be denoted as the extraordinary and ordinary indices and the calculated results are compared below with the observed values.

Index	Calculated	Observed
n_ϵ	1·468	1·486
n_0	1·672	1·658

[1] See Wasastjerna and also Bragg (*loc. cit.*).

The crystal structure of aragonite is slightly different but most of the above considerations apply to a high degree of approximation to this form of $CaCO_3$ as well. The carbonate group preserves its shape and dimensions and is accordingly the seat of birefringence as in the previous case. This crystal is biaxial but two of the principal refractive indices are very nearly equal to one another and we may therefore consider it as uniaxial as an approximation. Once this assumption is made, the only point in respect of which aragonite differs from calcite will be in the matter of its molecular volume $\frac{M}{\sigma}$, which in this case is 34·01. Accordingly $4\pi\nu_1\alpha_1$ will be 0·175 and $4\pi\nu_3\alpha_3$ will be 0·873 instead of the old values. The values of $C_3^{\perp}$ and $C_3^{\parallel}$ are however unaltered as we go from calcite to aragonite. Substituting these constants in turn in (2), we get the corresponding refractive indices and these are compared below with the observed values.

Index	Calculated	Observed
$n_{\perp}$	1·502	1·530
$n_{\parallel}$	1·726	1·681
$n_{\parallel}$	1·726	1·686

These calculations for calcite and aragonite were originally performed by Bragg by adopting a slightly different procedure, the principle underlying which is, however, the same as has been outlined above. We have now taken account of the influence of only the nearest neighbours around each oxygen atom. In a rigorous solution, the effect of all the neighbours has to be taken into account. Such a process will become very complicated. Bragg has made further assumptions and extended the calculations so as to include the effect of some more neighbours and has shown that a better fit between the calculated and observed values may be obtained.

Similar methods for calculating the natural birefringence have been adopted by Zachariasen[1] in the case of $NaHCO_3$

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[1] Jour. Chem. Phys., *1*, 640 (1933).

crystals and Hendricks and others[1] in some forms of ammonium nitrate crystals. The situation may be expected to be even simpler in molecular lattices such as are found in the region of organic crystals. It may now be said without any doubt that the natural birefringence exhibited by organic crystals will be determined firstly by the optical anisotropy of the molecule itself and secondly by the manner in which the various molecules that constitute the crystal are oriented with respect to one another. Numerous attempts have been made to connect the optical properties of the individual molecules with the optical properties of the crystal, as a whole, taking into consideration the known crystal structures.[2] In certain cases, the crystal structures have also been arrived at by working in the reverse direction. Before a brief review is made of these attempts, it may be mentioned that the problem is somewhat complicated on account of the presence of disturbing factors such as the mutual influence between the optic moments induced in the neighbouring molecules. A rigorous solution of the problem is therefore not easy of obtaining. Nevertheless, qualitative relationships which are based on considerations put forward in the foregoing chapter have been of immense use in the recent years in unravelling the crystal structures of numerous organic crystals. As an example, we may cite the two extreme cases of the long chain and ring-shaped molecules. It is easy to see that in the former case, the mutual influence of the doublets induced in the various atoms lying along the length of the chain is such as to enhance the refractivity of the molecule when the field is incident along the chain and diminish it when the field is incident along directions normal thereto. Consequently, if we are dealing with a crystal consisting of long chain molecules in which the lengths are arranged more or less parallel to one another, it is easy to identify, from a knowledge of the crystalline birefringence, the direction along which the lengths

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[1] Z. Krist., *85*, 143 (1933).

[2] S. Bhagavantam, Proc. Roy. Soc., *124*, 545 (1929); Ind. Jour. Phys., *4*, 1 (1929); K. S. Krishnan and S. Banerjee, Phil. Trans., *234*, 265 (1935); S. B. Hendricks and W. E. Derning, Z. Krist., *91*, 290 (1935); and several others.

of the molecules lie. This will be identical with the direction of maximum refractive index. On the other hand, if the crystal consists of ring-shaped or plane molecules so arranged that their planes are all parallel to one another, from a knowledge of the refractive indices of the crystal, this plane is easily identified as it should also contain the directions of maximum refractive index. The mutual influence of the various doublets in a molecule like benzene or naphthalene is such as to result in the refractive index normal to the plane of the rings being lowest. This conclusion is verified in a large number of organic crystals possessing known structures. It has been realized in recent years that such a procedure is of immense value as a preliminary to the study of crystal structure by the method of X-ray analysis. Table XVI is due to Bernal and illustrates the general relationships between birefringence and crystalline structure in organic compounds.

The relationships between double refraction and crystal structure in inorganic crystals have also been treated in a semi-empirical manner by Wooster.[1] Structures have been divided into types which are characterized by certain degrees of double refraction. These are shown in Table XVII. Even in this empirical classification, one can see that the general principles laid down in the foregoing are operating in all classes of crystals except the last one.

Electric Birefringence.—Most of the known liquids and gases, when placed in an electric field, exhibit a feeble birefringence. The behaviour of the medium in the presence of the field is exactly analogous to that of a uniaxial crystal with its optic axis parallel to the direction of the field. This phenomenon was first discovered by Kerr[2] and is now known as the Kerr effect. It has been found experimentally that the phase difference between the two principal components of the light beam is given by $KlE^2\lambda$ where λ is the wave-length of the light used, K is a constant characteristic of the substance, l is the length of the column of the medium in the electric field through

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[1] Z. Krist., *80*, 495 (1931).
[2] Phil. Mag., *50*, 337 (1875).

Table XVI

Relation between Crystal Structure and Optical Properties: Molecular Crystals

	Arrangements of Molecules	Optical Properties of Crystal	Conclusion	Examples
1	Molecule almost isotropic ..	Crystal almost isotropic ..	No information ..	Pentaerythritol, sugars.
2	Molecule rod shaped with one large and two small refractive indices.	....	....	....
2*a*	Rods almost parallel to one direction.	Crystal with +ve birefringence	Directions of rods fixed as that of greatest refractive index.	Paraffins, normal alcohols and acids.
2*b*	Rods not parallel to any direction but lying in one plane.	Crystal with −ve birefringence	Plane of rods fixed as normal to least refractive index.	Octadecyl ammonium chloride.
2*c*	Rods inclined in all directions	Crystal almost isotropic ..	Molecules cannot be arranged as in 2*a* and 2*b*.	Solid CO_2.
3	Molecules plane with two large and one small refractive index. Usually ring molecules.	....	....	....
3*a*	Planes parallel ..	Crystal with −ve birefringence	Planes normal to direction of least refractive index.	Ammonium oxalate, naphthalene, anthraquinone.
3*b*	Planes inclined but all parallel to a line.	Crystal with +ve birefringence	All planes include direction of greater birefringence.	Urea, benzene, spirohydantoin.
3*c*	Planes inclined in all directions	Crystal almost isotropic ..	Molecules cannot be arranged as in 3*a* or 3*b*.	Succinimide, hydroquinone.

TABLE XVII

Relation between Crystal Structure and Optical Properties: Inorganic Crystals

No.	Type of crystal structure	Nature of crystalline birefringence	Examples
1	Layer lattices ..	Strong negative double refraction except when the substance contains hydroxyl ions.	PbO_2, CdI_2, mica, etc.
2	Chain lattices ..	Strong positive double refraction when the chain is parallel to the optic axis.	HgS, Se.
3	Structures with strongly asymmetric groups.	Large double refraction.	CO_3, NO_3, N_3, etc.
4	Structures with symmetrical groups.	Low double refraction.	SO_4, ClO_4, SiO_4, etc.
5	Lattices consisting of three dimensional network.	Do.	Quartz, Felspar, etc.
6	Certain iron and titanium bearing substances.	High double refraction which is not due to marked asymmetry in the crystal structure.	TiO_2, Fe_2O_3, etc.

which the light passes and E is the strength of the electric field in electrostatic units. If the principal refractive indices[1] are n_p and n_s, the phase difference may also be written as $l(n_p-n_s)$. Equating the two we have

$$K = \frac{n_p - n_s}{\lambda E^2}.$$

K is dependent to some extent on the wave-length, the density and the temperature of the substance and has been customarily named the Kerr constant of the substance.

There have been many attempts at explaining the mechanism of this phenomenon. The first successful one was based on the

[1] n_p and n_s are the indices obtained when the electric vector of the incident light is respectively parallel and perpendicular to the direction of the electric field.

idea of optically anisotropic molecules. It was given by Langevin.[1] The electric field is supposed to exercise an orientative influence on the molecules owing to the interaction between the field and the induced moments. As the molecules themselves possess an intrinsic optical anisotropy, the ordered orientation which lasts as long as the field lasts, results in the fluid as a whole becoming optically anisotropic with the direction of the field as an axis of symmetry. Born,[2] later, introduced the effect of the possession of a permanent electric moment by the molecules and modified the expressions given by Langevin for the Kerr constant. We shall now consider in detail the Langevin-Born theory of electric birefringence and show that it is intimately connected with the subject of optical anisotropy of molecules. Let the static electric field be represented by E_0 along OZ (Fig. 5). The potential energy of a molecule θ, φ, ψ in the field is composed of two parts. The first part arises from the possession of a permanent electric moment whose components along the principal optic axes of the molecule may be denoted by μ_1, μ_2, μ_3 and the second part arises from the induced moments. The potential energy may be written as

$$U = -(\mu_1 E_0 \cos ZX' + \mu_2 E_0 \cos ZY' + \mu_3 E_0 \cos ZZ') \\ -\tfrac{1}{2}\{\bar{A}(E_0 \cos ZX')^2 + \bar{B}(E_0 \cos ZY')^2 + \bar{C}(E_0 \cos ZZ')^2\}.$$

$\bar{A}$, $\bar{B}$ and $\bar{C}$ represent the principal electric moments induced in the molecule by a unit electric field acting respectively along the three principal axes of the ellipsoid of optical polarizability. The probability that a molecule may be found in a solid angle $d\omega$ may now be written as

$$C \cdot e^{-U/kT} \cdot \sin\theta \, d\theta d\varphi d\psi .$$

If a light wave of amplitude E_z in the direction of OZ is incident in the direction OY, the resultant moment induced in the direction OZ may be written as[3]

$$p_z = (A \cos^2 ZX' + B \cos^2 ZY' + C \cos^2 ZZ')E_z.$$

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[1] Jour. d. Phys., 7, 249 (1910).

[2] Ann. d. Phys., 55, 177 (1918).

[3] See (17) of chapter III and the subsequent treatment.

Similarly the component along OX of the moment induced in each one of these molecules by a light wave of amplitude E_x along OX may be written as

$$p_x = (A\cos^2 XX' + B\cos^2 XY' + C\cos^2 XZ')E_x.$$

The average moment induced per molecule per unit field in the direction OZ, when the vibration vector in the incident field is in the direction OZ, may be denoted by α_z and is given by [1]

$$\alpha_z = \frac{C\int e^{-U/kT} \,.\, p_z \,.\, \sin\theta \; d\theta d\varphi d\psi}{E_z C\int e^{-U/kT} \,.\, \sin\theta \; d\theta d\varphi d\psi}$$

Similarly α_x is given by

$$\alpha_x = \frac{C\int e^{-U/kT} \,.\, p_x \,.\, \sin\theta \; d\theta d\varphi d\psi}{E_x C\int e^{-U/kT} \,.\, \sin\theta \; d\theta d\varphi d\psi}.$$

By separating out the constant factor $\frac{A+B+C}{3}$ and neglecting higher powers of U/kT in the exponential expansion on the assumption that U/kT is small, the integrals may be evaluated and the following results obtained.

$$\alpha_z = \frac{A+B+C}{3} + \frac{E_0^2}{2}\left\{\frac{2}{45kT}[(\bar{A}-\bar{B})(A-B)+(\bar{B}-\bar{C})(B-C)+(\bar{C}-\bar{A})(C-A)] + \frac{2}{45k^2T^2}[(\mu_1^2-\mu_2^2)(A-B)+(\mu_2^2-\mu_3^2)(B-C)+(\mu_3^2-\mu_1^2)(C-A)]\right\},$$

$$\alpha_x = \frac{A+B+C}{3} - \frac{E_0^2}{2}\left\{\frac{1}{45kT}[(\bar{A}-\bar{B})(A-B)+(\bar{B}-\bar{C})(B-C)+(\bar{C}-\bar{A})(C-A)] + \frac{1}{45k^2T^2}[(\mu_1^2-\mu_2^2)(A-B)+(\mu_2^2-\mu_3^2)(B-C)+(\mu_3^2-\mu_1^2)(C-A)]\right\}.$$

[1] Integration refers to all the three variables, θ, ϕ and ψ as before.

If we use the symbols Θ_1 for $\frac{1}{45kT}$ $[(\bar{A}-\bar{B})(A-B)\ldots\ldots$, etc.] and Θ_2 for $\frac{1}{45k^2T^2}$ $[(\mu_1^2-\mu_2^2)(A-B)\ldots\ldots$, etc.], we have

$$\alpha_z = \alpha + \frac{E_0^2}{2}[2\{\Theta_1+\Theta_2\}] \text{ and } \alpha_x = \alpha - \frac{E_0^2}{2}[\Theta_1+\Theta_2]. \quad .. \quad (3)$$

The following relationships also hold.

$$\frac{n_p^2-1}{n_p^2+2} = \frac{4\pi\nu\alpha_z}{3}; \quad \frac{n_s^2-1}{n_s^2+2} = \frac{4\pi\nu\alpha_x}{3}; \quad \frac{n_0^2-1}{n_0^2+2} = \frac{4\pi\nu\alpha}{3}. \quad (4)$$

The effective field E_0 is related to the external field E by the relation

$$E_0 = E\left(\frac{\varepsilon+2}{3}\right).$$

Differentiating the last of the relationships in (4), we have

$$\frac{\triangle n_0}{n_0} = \frac{(n_0^2-1)(n_0^2+2)}{6n_0^2}\left(\frac{\triangle\alpha}{\alpha}+\frac{\triangle\nu}{\nu}\right).$$

Substituting for $\triangle\alpha$ from equation (3) and remembering that the effective field is $E\left(\frac{\varepsilon+2}{3}\right)$, we have

$$\frac{n_p-n_0}{n_0} = \frac{(n_0^2-1)(n_0^2+2)}{6n_0^2}\left\{\frac{\triangle\nu}{\nu}+E^2\left(\frac{\varepsilon+2}{3}\right)^2\frac{\Theta_1+\Theta_2}{\alpha}\right\},$$

$$\frac{n_s-n_0}{n_0} = \frac{(n_0^2-1)(n_0^2+2)}{6n_0^2}\left\{\frac{\triangle\nu}{\nu}-\frac{E^2}{2}\left(\frac{\varepsilon+2}{3}\right)^2\frac{\Theta_1+\Theta_2}{\alpha}\right\}. \quad .. \quad (5)$$

We now obtain (6) by combining the two equations numbered (5). The value of K is then given by (7).

$$\frac{n_p-n_s}{n_0} = \frac{(n_0^2-1)(n_0^2+2)}{6n_0^2}\cdot\frac{E^2}{2}\left\{3\left(\frac{\varepsilon+2}{3}\right)^2\frac{\Theta_1+\Theta_2}{\alpha}\right\}, \quad .. \quad (6)$$

$$K = \frac{n_p-n_s}{\lambda E^2} = \frac{(n_0^2+2)^2\pi\nu}{3\lambda n_0}\left(\frac{\varepsilon+2}{3}\right)^2[\Theta_1+\Theta_2]. \quad .. \quad (7)$$

In the case of a gas, n_0 and ε are both very nearly equal to unity and equation (7) reduces to (8).

$$K = \frac{3\pi\nu}{\lambda}[\Theta_1+\Theta_2] = K_1+K_2. \quad .. \quad .. \quad .. \quad (8)$$

The two terms K_1 and K_2 may be denoted as the anisotropic and dipole ones respectively. If the molecules are electrically non-polar, the second term vanishes and if the molecules are also optically spherical, both the terms vanish. A further simplification may be effected in the following manner by expressing Θ_1 and Θ_2 in terms of the optical anisotropy of the molecule. Let us assume in the first instance that the molecule is electrically non-polar and that

$$\frac{\bar{A}}{A} = \frac{\bar{B}}{B} = \frac{\bar{C}}{C} = \frac{\varepsilon - 1}{n_0^2 - 1}, \qquad \cdots \qquad \cdots \qquad (9)$$

where ε is the dielectric constant and n is the refractive index. The expression for Θ_1 reduces to

$$\frac{1}{45kT} \cdot \frac{\varepsilon - 1}{n_0^2 - 1} [(A-B)^2 + (B-C)^2 + (C-A)^2].$$

Substituting $2\delta\,(A+B+C)^2$ for $(A-B)^2+(B-C)^2+(C-A)^2$ and simplifying, we have

$$\Theta_1 = \frac{(\varepsilon - 1)(n_0^2 - 1)}{8kT\pi^2\nu^2} \cdot \frac{\varrho}{6 - 7\varrho}. \qquad \cdots \qquad \cdots \qquad (10)$$

Therefore

$$K = \frac{3(\varepsilon - 1)(n_0 - 1)}{4\pi kT\nu\lambda} \cdot \frac{\varrho}{6 - 7\varrho}. \qquad \cdots \qquad \cdots \qquad (11)$$

This equation, first deduced by Raman and Krishnan,[1] shows the relationship between the Kerr constant and the depolarization factor for a non-polar gas. In the case of electrically polar molecules, Θ_2 does not vanish and has to be evaluated. Θ_1 is usually small in comparison with Θ_2 and the above procedure may still be adopted for evaluating it except that ε should now stand for the induced part of the dielectric constant alone, the contributions from the permanent moments being entirely omitted. Θ_2 may, in general, be evaluated only if we know the values of μ_1, μ_2 and μ_3. In the simple case where the optical ellipsoid is a spheroid ($A = B \neq C$) and the permanent moment is either parallel to the axis of the spheroid or is inclined to it at some known angle θ, Θ_2 can be evaluated

[1] Phil. Mag., *3*, 713 (1927).

in terms of the depolarization factor. Putting A=B and $\mu_3^2 = \mu^2 \cos^2\theta$ and $\mu_1^2+\mu_2^2 = \mu^2 \sin^2\theta$, we have

$$\Theta_2 = \frac{\mu^2}{45k^2T^2}[(C-A)(2\cos^2\theta-\sin^2\theta)]$$

$$= \pm\frac{(n_0-1)\mu^2}{30\pi\nu k^2T^2}(2\cos^2\theta-\sin^2\theta)\sqrt{\frac{5\varrho}{6-7\varrho}}. \qquad .. \quad (12)$$

In deriving (12), use is made of (2) of chapter IV. The + or − sign should be taken according as the optical ellipsoid is prolate or oblate, i.e., according as $C \gtrless A=B$. We thus arrive at the most important result that if the permanent electric moment of the molecule lies along directions of smaller optical polarizability of the molecule, then the medium should exhibit a negative Kerr constant. An example of this type is chloroform. This substance exhibits a negative Kerr effect and this is due to the fact that the optical ellipsoid of the molecule is a spheroid with a minimum polarizability along the CH line. The axis of the permanent doublet may also be taken to be in this direction and hence the negative Kerr constant stands satisfactorily explained in terms of the Langevin-Born theory.

In the case of liquids, we have the relation

$$\frac{\overline{A}'}{A'} = \frac{\overline{B}'}{B'} = \frac{\overline{C}'}{C'} = \frac{\varepsilon-1}{\varepsilon+2}\Big/\frac{n_0^2-1}{n_0^2+2},$$

instead of (9) and the expression for Θ_1 reduces to (13).

$$\Theta_1 = \frac{1}{45kT}\frac{\varepsilon-1}{\varepsilon-2}\cdot\frac{n_0^2+2}{n_0^2-1}[(A'-B')^2+(B'-C')^2+(C'-A')^2]. \qquad .. \quad (13)$$

If in the first instance we consider non-polar liquids, Θ_2 vanishes and

$$\varrho_{\text{liq.}} = \frac{6[(A'-B')^2+(B'-C')^2+(C'-A')^2]}{10kT\beta\nu(A'+B'+C')^2+7[(A'-B')^2+(B'-C')^2+(C'-A')^2]},$$

$$\frac{n_0^2-1}{n_0^2+2} = \frac{4\pi\nu}{3}\cdot\frac{A'+B'+C'}{3},$$

giving

$$\Theta_1 = \frac{9\beta(\varepsilon-1)(n_0^2-1)}{8\pi^2\nu(\varepsilon+2)(n_0^2+2)}\cdot\frac{\varrho_{\text{liq.}}}{6-7\varrho_{\text{liq}}}. \qquad .. \quad (14)$$

With the help of (18) of chapter V, it may easily be seen that this reduces to (10) if the medium is gaseous (ε and n_0 nearly equal to unity). ϱ in (10) refers to the depolarization factor in the gaseous state. The Kerr constant of a non-polar liquid is therefore given as

$$K = \frac{\beta(n_0^2-1)(n_0^2+2)(\varepsilon-1)(\varepsilon+2)}{24\pi n_0\lambda} \cdot \frac{\varrho_{liq.}}{6-7\varrho_{liq.}} \cdot \quad .. \quad (15)$$

In the case of polar liquids, the considerations, which are complicated, are to some extent empirical. Reference may be made to a paper by Raman and Krishnan.[1] In the following Tables, data regarding the Kerr constants of a few typical vapours and of non-polar liquids are given. The wave-length has been assumed to be λ5460 A.U. in the case of the liquids.

TABLE XVIII

Kerr Constant of Gases and Vapours

Gas or Vapour	$(\epsilon-1) \times 10^6$	$\lambda \times 10^8$	$(n_0-1) \times 10^6$	$\rho \times 100$	$\mu \times 10^{18}$	θ	T	$K_1 \times 10^{10}$	$K_2 \times 10^{10}$	$K \times 10^{10}$ Calc.	$K \times 10^{10}$ obs.
Hydrogen	264	4550	141 4	2 6	0	..	308	0·008	0	0·008	<0·01
Carbon dioxide	976	,,	451·0*	9·7	0	..	308	0·37	0	0·37	0·34
,, .	,,	5460	450·6	9·7	0		291	0·32	0	0 32	0·26
Nitrogen .	606	,,	298·2	3·6	0		308	0·043	0	0·043	0·057
Nitrous oxide ..	1060	,,	510·0	12·5	0	..	299	0·52	0	0·52	0·56
Carbon disulphide .	2900	,,	1485*	11·5	0	..	330	3·40	0	3 40	3·85
Acetylene	1243	,,	605·1	4·5	0	..	298	0·24	0	0 24	0·34
Chlorine ..	1570	,,	784·0	4·1	0	..	297	0·35	0	0·35	0·42
Benzene ..	3000	,,	1820*	4·5	0		387	1·32	0	1·32	1·02
Oxygen ..	547	6500	269·2	6·5	0	.	273	0·062	0	0·062	0·069
Hydrogen chloride ..	1040	5460	448·0	0 7	1·03	0	291	0·022	0·84	0·86	1·05
Ammonia ..	768	,,	387·0	1·0	1·44	0	291	0·020	1·69	1·71	0·64
Chloroform ..	4200	,,	1442·0*	1·8	1·05	0	363	0·60	—2·91	−2·31	—1·37

* n_0 refers to λ5893.

It may be mentioned here that with the help of the optical constants obtained in the vapour state, the Kerr constant to be expected in the corresponding liquid may easily be evaluated. The validity of such calculations rests on the validity of (18) of chapter V. It has already been mentioned that (18) of chapter V does not hold good in many cases and that Raman

[1] Phil. Mag., *3*, 724 (1927).

TABLE XIX

Kerr Constant of Non-polar Liquids

Liquid	Formula	ϵ	n_0	$\rho_{\text{liq.}}$	$\beta \times 10^6$ per atm.	$K \times 10^7$ calc.	$K \times 10^7$ obs.
Hexane ..	C_6H_{14}	1·729	1·372	0·0995	159	0·049	{ 0·045 0·056
Carbon disulphide	CS_2	2·593	1·656	0·62	95	3·11	3·23
Benzene ..	C_6H_6	2·284	1·495	0·42	95	0·60	0·59

and Krishnan have, in this connection, introduced the idea of an anisotropic optical polarization field. In order that (15) may be successfully applied, we must therefore use either the observed $\varrho_{\text{liq.}}$ or the corresponding value calculated from ϱ_{gas} and the dimensions of the molecule on the basis of Raman-Krishnan theory.

Magnetic Birefringence.—Cotton and Mouton observed for the first time in 1907 that some liquids, when placed in a magnetic field, exhibit a feeble birefringence. This effect, known as the Cotton-Mouton effect, is the magneto-optic analogue of the Kerr effect. The behaviour of the liquid in the presence of a magnetic field is again like that of a uniaxial crystal with its optic axis parallel to the direction of the field. We may introduce a quantity C given by

$$C = \frac{n_p - n_s}{\lambda H^2}.$$

C is again dependent to some extent on the wave-length, the density and the temperature, and is termed the Cotton-Mouton constant. If *a*, *b* and *c* are the principal diamagnetic moments induced by a unit magnetic field acting along the respective principal axes, adopting a reasoning which is similar to that adopted in the case of Kerr effect, we can arrive at the following equation.

$$C = \frac{n_p - n_s}{\lambda H^2} = \frac{(n_0^2 - 1)(n_0^2 + 2)}{4\lambda n} \cdot \frac{\Theta_1}{\alpha'}, \quad \ldots \quad \ldots \quad \ldots \quad (16)$$

where

$$\Theta_1 = \frac{1}{45kT} [(a-b)(A' - B') + (b-c)(B' - C') + (c-a)(C' - A')].$$

Equation (16) is analogous to (6) of the section on Kerr effect. It may, however, be noted that the term Θ_2 of (6), which arises only in the case of molecules possessing a permanent electric moment, is not present in (16). This is a consequence of the fact that we are dealing with molecules which do not possess a permanent magnetic moment. The effective magnetic field and the actual field do not appreciably differ from each other in diamagnetic media and hence no term analogous to $\left(\frac{\varepsilon+2}{3}\right)^2$ is present in this case. Dashed letters are not used for the magnetic moments for the same reason, although expression (16) refers to the liquid state. (16) may alternatively be written, by replacing α' with $\frac{A'+B'+C'}{3}$, in the following manner as has often been done in the literature.

$$C = \frac{n_p - n_s}{\lambda H^2} = \frac{(n_0^2-1)(n_0^2+2)}{60kT\lambda n} \times$$
$$\frac{[(a-b)(A'-B')+(b-c)(B'-C')+(c-a)(C'-A')]}{A'+B'+C'} \quad \ldots \quad (17)$$

It is easily seen that the Cotton-Mouton constant vanishes if the molecule is either magnetically or optically isotropic or both. A direct correlation of the Cotton-Mouton constant with the optical anisotropy, in the general case, is not possible, but in a simple case where $A'=B'$ and $a=b$, it may be effected. We then have

$$C = \frac{(n_0^2-1)(n_0^2+2)}{60kT\lambda n_0} \cdot 2\,(c-a) \cdot \frac{C'-A'}{C'+2A'} \cdot \quad \ldots \quad (18)$$

We also have the following relations, if χ stands for the gramme susceptibility.

$$\frac{C'-A'}{C'+2A'} = \sqrt{\delta_{\text{liq}}} \text{ and } \frac{C+2a}{3} = \frac{\chi \cdot M}{N}.$$

Certain very interesting conclusions emerge out of (18). In diamagnetic substances, c and a are always negative and it is easily seen that C is always negative if $c-a$ has the same sign as $C'-A'$. This may be interpreted by saying that if the directions of maximum optical polarizability and the numerically

maximum magnetic susceptibility coincide, the substance will exhibit a negative Cotton-Mouton effect. Extensive investigations of Ramanadham[1] have shown that a great majority of the aliphatic compounds, particularly the saturated ones, come under this class. On the other hand, C is positive if $c-a$ and $C'-A'$ have opposite signs. This implies that a positive Cotton-Mouton effect will result, if the direction of the maximum optical polarizability coincides with that of the numerically minimum magnetic susceptibility. Most of the organic compounds of the aromatic class come under this category. Benzene itself and all its derivatives are typical examples of substances exhibiting strong positive magnetic double refraction. Direct experimental confirmation of these relationships[2] is also made available by first working with typical organic crystals in respect of their optical and magnetic properties and then with their solutions in respect of their magnetic birefringence.[3] Crystals of naphthalene afford a striking example of the class of substances in which the directions of maximum optical polarizability and minimum magnetic susceptibility coincide. Molten naphthalene and solutions of naphthalene in carbon tetrachloride[4], accordingly, exhibit strong positive Cotton-Mouton effect. A striking illustration of the other class of substances is available in iodoform.[5] The direction of the maximum optical polarizability coincides with that of the maximum magnetic susceptibility and we should therefore expect solutions of this substance

[1] Ind. Jour. Phys., *4*, 15 and 109 (1929).

[2] The conclusions generally hold good in many other unsymmetrical cases also. For a rigorous treatment of such a case, we may, however, consider the more general expression (17) in a similar manner.

[3] S. Bhagavantam, Ind. Jour. Phys., *4*, 1 (1929).

[4] Carbon tetrachloride, being symmetrical, is a neutral substance from the point of view of magnetic birefringence.

[5] In both naphthalene and iodoform crystals, the molecules are all situated in such a way that their principal axes are more or less parallel to each other and hence we could assume that the relative orientations of the principal axes of the molecule are nearly the same as those that are found for the crystal. In more complicated cases, relative orientations of the molecules present in the particular case have to be taken into account.

to exhibit negative Cotton-Mouton effect. We have no data in respect of this, but both the analogous cases of chloroform and bromoform exhibit negative Cotton-Mouton effect. It is not possible to verify (18) experimentally unless the values of c and a are known. As such we shall, in a few typical cases of spheroidal symmetry for which $\delta_{liq.}$, χ and C are known, calculate the values of c and a. The results for three liquids are given in the following Table.

TABLE XX

Cotton-Mouton Constant of Liquids

Substance	$\delta \times 10^3$	T	$\chi \times 10^6$	n_0	$C \times 10^{14}$	$c \times 10^{28}$	$a \times 10^{28}$
Benzene . .	18·0	303	−0·71	1·495	59·0	1·48	0·63
Carbon disulphide . .	72·4	,,	−0·54	1·656	−49·6	0·85	0·59
Chloroform . .	9·3	,,	−0·50	1·453	− 7·0	0·93	1·09
Benzene vapour (λ5460) . .	39·6	363	same as liquid reduced to N.T.P.	1·00182	0·250	1·54	0·60

Many other substances have been studied from this viewpoint and results of great significance obtained. For a more detailed discussion of this subject, reference may be made to a recent article by Schutz.[1] Recently, König[2] has obtained the Cotton-Mouton effect in benzene vapour. His result is also quoted in the last row of Table XX. Equation (18) applies to the case of vapour if the dashes on the optic moments are omitted. The value of δ appropriate to the vapour state has to be used. Assuming that the mean molar magnetic susceptibility remains unaltered as we pass from the liquid to the vapour state in benzene, we may similarly calculate the principal magnetic moments. The values so calculated and given in the last two columns agree very well with those obtained in the liquid state. This result shows that not only the mean susceptibility but also the magnetic anisotropy of the benzene molecule remains unaltered as we pass from the liquid to the vapour state.

[1] *Handbuch Der Experimental Physik, 16,* 210 (1936).

[2] Ann. d. Phys., *31,* 289 (1938).

Mechanical Birefringence.—Maxwell first observed that mechanical agitation induces birefringence in an otherwise isotropic liquid. This effect is easily demonstrated in the following manner. If a liquid is contained in the gap between two coaxial cylinders and if the inner one is made to rapidly rotate, the liquid exhibits a feeble birefringence. The behaviour of the liquid as a whole is analogous to that of a uniaxial crystal. This phenomenon, which may be denoted by the term mechanical birefringence, is now known as the Maxwell effect. A simple arrangement, originally suggested by Maxwell, has been recently adopted by Vorlander and Walter[1] who studied the Maxwell effect in a large number of liquids. In their experiments, these authors passed a beam of plane polarized light through the liquid, contained between two coaxial cylinders, in a direction parallel to the axis of the cylinders. The inner cylinder is rotated at a high speed and the birefringence exhibited by the liquid is measured by suitable optical methods. The experimental arrangements of Vorlander and Walter have been criticized by Sadron[2] on the ground that the former authors adopted speeds of rotation so excessive that turbulence may have set in. Sadron repeated the experiments in a few typical liquids with improved apparatus and lower velocities and obtained results somewhat different from those obtained by Vorlander and Walter.

An obvious conclusion which may be drawn from the work of these authors is that Maxwell effect is observable in numerous common liquids in the pure state and is therefore a property of the liquid itself. That this phenomenon is also intimately connected with the optical anisotropy of the molecules and that it may be explained in a satisfactory manner on lines similar to those adopted by Langevin and Born in the case of electric and magnetic birefringence, were first pointed out by Raman and Krishnan[3]. Theory of the Maxwell effect as given by Raman and Krishnan will now be outlined.

[1] Z. f. Phys. Chem., *118*, 1 (1925).
[2] Jour. d. Phys., *7*, 263 (1936).
[3] Phil. Mag., *4*, 769 (1928).

The birefringence is regarded as arising from the optical anisotropy of the molecules as in the electric and magnetic cases. The agency which causes the molecules to orient in specific directions in this case is, however, the mechanical stress in the fluid, different parts of which are in relative motion with respect to one another. The viscous forces, called into play, act on the non-spherical molecules and orient them. This orientation lasts as long as the relative motion persists and the liquid as a whole exhibits birefringence.

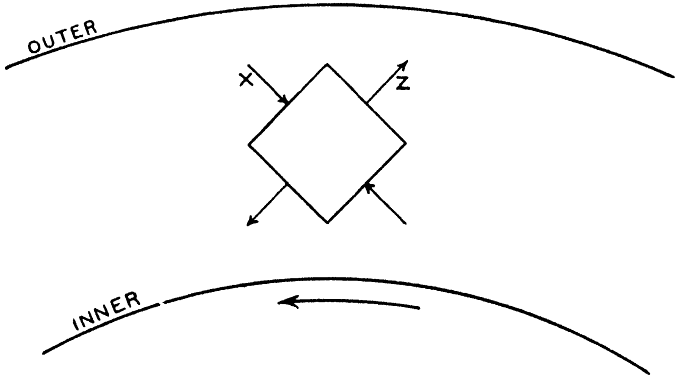


FIG. 18.

In figure 18, which represents a section perpendicular to the common axis of the cylinders, the inner cylinder is rotating in the direction of the arrow and the outer one remains fixed. The tangential viscous forces, called into play, may be regarded as composed of two sets of stresses, one set consisting of tensions and the other set of pressures, acting along two directions which are mutually perpendicular and inclined at 45° to the line of flow. If v is the linear velocity at the surface of the inner cylinder and if c is the clearance between the cylinders, $\frac{v}{c}$ is the velocity gradient and the viscous force called into play is $\eta \frac{v}{c}$ per unit area, where η is the viscosity of the medium. This is equivalent to a tension of $\eta \frac{v}{c}$ per unit area and a pressure of $\eta \frac{v}{c}$

per unit area. Orientation now takes place in such a manner that the longest dimension of the molecule tends to lie along the axis of tension. An equilibrium between this tendency and thermal agitation of the molecules sets in and the resulting state of statistical equilibrium gives rise to birefringence.

The direction of tension, the direction of pressure and an axis parallel to the axis of rotation are chosen as the Z, X and Y axes respectively. We now consider a molecule whose principal geometric axes have an orientation θ, φ and ψ in the above system of co-ordinates (Fig. 5). We now assume that the potential energy of such a molecule is proportional to $\eta \cdot \frac{v}{c} \cdot \frac{1}{\nu}$, the coefficient of proportionality being a function of θ, φ and ψ. ν is the number of molecules per c.c. of the medium. We write the potential energy as

$$U = -(\omega_1 \cos^2 ZX' + \omega_2 \cos^2 ZY' + \omega_3 \cos^2 ZZ')\eta \cdot \frac{v}{c} \cdot \frac{1}{\nu}.$$

The proportionality factor is so chosen that it does not change sign if the molecule is rotated through 180°. ω_1, ω_2 and ω_3 are constants to be determined.

The probability of a molecule being found in a solid angle $d\omega$ is given by

$$C \,.\, e^{-U/kT} \sin\theta \, d\theta d\varphi d\psi.$$

In the oriented state, the average potential energy per molecule is

$$\bar{U} = \frac{C\int e^{-U/kT} \,.\, U \,.\, \sin\theta \, d\theta d\varphi d\psi}{C\int e^{-U/kT} \sin\theta \, d\theta d\varphi d\psi}$$

$$= -\frac{(\omega_1+\omega_2+\omega_3)}{3}\eta\frac{v}{c}\cdot\frac{1}{\nu} - \frac{2}{45kT}\Big[(\omega_1-\omega_2)^2+(\omega_2-\omega_3)^2 + (\omega_3-\omega_1)^2\Big]\left(\eta\cdot\frac{v}{c}\cdot\frac{1}{\nu}\right)^2.$$

If, on the other hand, the molecules are oriented entirely at random, the average potential energy per molecule will be given by

$$\bar{U}_0 = \frac{\int U \sin\theta \, d\theta d\varphi d\psi}{\int \sin\theta \, d\theta d\varphi d\psi} = \frac{-(\omega_1+\omega_2+\omega_3)}{3}\eta \,.\, \frac{v}{c} \,.\, \frac{1}{\nu}.$$

The difference $\bar{U}_0-\bar{U}$ multiplied by ν gives the diminution of potential energy per unit volume consequent on orienting the molecules contained in it and is equal to

$$\left(\bar{U}_0-\bar{U}\right)\nu = \frac{2}{45kT}\left[(\omega_1-\omega_2)^2+(\omega_2-\omega_3)^2+(\omega_3-\omega_1)^2\right]\left(\eta\cdot\frac{v}{c}\right)^2\cdot\frac{1}{\nu}. \quad \ldots \quad \ldots \quad (19)$$

Making certain simplifying assumptions, Raman and Krishnan have calculated this quantity in a slightly different manner. If the molecules are arbitrarily oriented, it may easily be shown that the average effective length of the molecule in any direction, say the Z direction, is simply

$$\frac{\bar{a}+\bar{b}+\bar{c}}{3}, \quad \ldots \quad \ldots \quad \ldots \quad (20)$$

where $\bar{a}$, $\bar{b}$ and $\bar{c}$ are the geometric dimensions of the molecules. On the other hand, under the action of tensions in the Z direction, the average length of each molecule in the Z direction will be

$$\frac{\int e^{-U/kT}(\bar{a}\cos^2 ZX'+\bar{b}\cos^2 ZY'+\bar{c}\cos^2 ZZ')\sin\theta\, d\theta d\varphi d\psi}{\int e^{-U/kT}\sin\theta\, d\theta d\varphi d\psi}$$

$$=\frac{\bar{a}+\bar{b}+\bar{c}}{3}+\frac{2}{45kT}\Big[(\omega_1-\omega_2)(\bar{a}-\bar{b})+(\omega_2-\omega_3)(\bar{b}-\bar{c})$$

$$+(\omega_3-\omega_1)(\bar{c}-\bar{a})\Big]\eta\cdot\frac{v}{c}\cdot\frac{1}{\nu}. \quad \ldots \quad (21)$$

The difference between (20) and (21) divided by (20) gives the effective expansion per unit length along the Z axis owing to the orientation of molecules under the action of a tension equal to $\eta\cdot\frac{v}{c}$ in this direction. The work done per unit volume by this tension is therefore given by

$$\tfrac{1}{2}\eta\cdot\frac{v}{c}\cdot\frac{2}{45kT}\times$$

$$\left[\frac{(\omega_1-\omega_2)(\bar{a}-\bar{b})+(\omega_2-\omega_3)(\bar{b}-\bar{c})+(\omega_3-\omega_1)(\bar{c}-\bar{a})}{\bar{a}+\bar{b}+\bar{c}}\right]\eta\cdot\frac{v}{c}\cdot\frac{1}{\nu}$$

$$\ldots \quad (22)$$

Equating this to (19), we have

$$\frac{3}{2}\left[\frac{(\omega_1-\omega_2)(\bar{a}-\bar{b})+(\omega_2-\omega_3)(\bar{b}-\bar{c})+(\omega_3-\omega_1)(\bar{c}-\bar{a})}{\bar{a}+\bar{b}+\bar{c}}\right]=$$

$$(\omega_1-\omega_2)^2+(\omega_2-\omega_3)^2+(\omega_3-\omega_1)^2.$$

A solution of this equation is

$$\frac{\omega_1-\omega_2}{\bar{a}-\bar{b}}=\frac{\omega_2-\omega_3}{\bar{b}-\bar{c}}=\frac{\omega_3-\omega_1}{\bar{c}-\bar{a}}=\frac{3}{2(\bar{a}+\bar{b}+\bar{c})}\ \ldots \quad (23)$$

The birefringence consequent on such an orientation may now be calculated by a procedure analogous to that adopted for the Kerr effect.

If light is incident along the Y axis and has an amplitude E_z in the direction of Z, then the moment induced in a molecule θ, φ, ψ in the Z direction is

$$p_z=(A'\cos^2 ZX'+B'\cos^2 ZY'+C'\cos^2 ZZ')E_z$$

and there are $C\int e^{-U/kT}\sin\theta\, d\theta d\varphi d\psi$ such molecules. The average moment α_z' induced per molecule per unit field in the Z direction is given as before by

$$\alpha_z'=\frac{C\int e^{-U/kT}\,p_z\sin\theta\, d\theta d\varphi d\psi}{E_z C\int e^{-U/kT}\sin\theta\, d\theta d\varphi d\psi}.$$

α_x' is given by a similar expression as in the case of Kerr effect. These integrals may be exponentially expanded and evaluated as before and α_z' and α_x' given as follows.

$$\alpha_z'=\frac{A'+B'+C'}{3}+2\Theta\eta\,.\frac{v}{c}\,.\frac{1}{\nu},$$

$$\alpha_x'=\frac{A'+B'+C'}{3}-\Theta\eta\,.\frac{v}{c}\,.\frac{1}{\nu}.$$

In these expressions

$$\Theta=\frac{1}{45kT}[(\omega_1-\omega_2)(A'-B')+(\omega_2-\omega_3)(B'-C')$$

$$+(\omega_3-\omega_1)(C'-A')]\ \ldots \quad (24)$$

and we get

$$\alpha_z'-\alpha_x'=3\Theta\eta\frac{v}{c}\,.\frac{1}{\nu}.$$

The effect of the compressions $\eta \frac{v}{c}$ along the X axis will result in an additional

$$\alpha_x' - \alpha_z' = -3\Theta\eta\frac{v}{c}\cdot\frac{1}{\nu}$$

and the net change in α is

$$\alpha_z' - \alpha_x' = 6\Theta\eta\frac{v}{c}\cdot\frac{1}{\nu}. \qquad \ldots \qquad \ldots \qquad (25)$$

Using the result contained in (25), we now get the following expression for $\frac{n_p - n_s}{n_0}$ by adopting the same procedure as has been adopted for deriving (6) of the section on Kerr effect.

$$\frac{n_p - n_s}{n_0} = \frac{(n_0^2-1)(n_0^2+2)}{6n_0^2}\cdot 6\left[\frac{\Theta}{\alpha'}\right]\eta\cdot\frac{v}{c}\cdot\frac{1}{\nu}.$$

Dashed letters have been used throughout for the optic moments as we are dealing with the liquid state.

If we define the Maxwell constant ∇ by the equation

$$\nabla = \frac{n_p - n_s}{\eta\cdot\frac{v}{c}},$$

we have

$$\nabla = \frac{(n_0^2-1)(n_0^2+2)}{n_0}\left[\frac{\Theta}{\alpha'}\right]\frac{1}{\nu}.$$

Substituting the value of Θ from (24) and $\frac{A'+B'+C'}{3}$ for α', we have

$$\nabla = \frac{(n_0^2-1)(n_0^2+2)}{15\eta_0 kT\nu}\times \frac{(\omega_1-\omega_2)(A'-B')+(\omega_2-\omega_3)(B'-C')+(\omega_3-\omega_1)(C'-A')}{A'+B'+C'}.$$

$(\omega_1-\omega_2)$ etc., may be replaced by the geometrical dimensions from (23) and we obtain

$$\nabla = \frac{(n_0^2-1)(n_0^2+2)}{10n_0 kT\nu}\times \frac{(\bar{a}-\bar{b})(A'-B')+(\bar{b}-\bar{c})(B'-C')+(\bar{c}-\bar{a})(C'-A')}{(\bar{a}+\bar{b}+\bar{c})(A'+B'+C')}. \qquad \ldots \qquad (26)$$

A number of important conclusions may be drawn from this result. The mechanical birefringence arises from the combined effect of a geometrical and optical anisotropy. If the molecule is either geometrically or optically spherically symmetrical or both, no mechanical birefringence should be expected. Higher viscosity helps the production of mechanical birefringence. The principal axes are mutually perpendicular to each other and are each inclined at 45° to the plane of sliding. The sign of birefringence may be either positive or negative according as if $\bar{a} > \bar{b} > \bar{c}$, $A' > B' > C'$ or $A' < B' < C'$. The former case is, however, to be expected more often than the latter. The birefringence does not explicitly depend on the wave-length but is not independent of it as it involves the refractive index which in its turn is a function of wave-length. Hence, a dispersion of birefringence should be expected. All these conclusions are supported by the experimental results obtained by Vorlander and Walter and by Sadron. An accurate quantitative comparison of the conclusions of the theory with experiment is, however, not possible as some of the data are wanting but an attempt is made in Table XXI in the case of a few liquids by making certain assumptions[1]. If the molecule possesses an axis of symmetry ($\bar{a} = \bar{b}$ and $A' = B'$), then (26) may be written as

$$\nabla = \pm \frac{(n_0^2-1)(n_0^2+2)}{10 n_0 k T \nu} \cdot \frac{2(\bar{c}-\bar{a})}{2\bar{a}+\bar{c}} \sqrt{\delta_{\text{liq}}} \quad .. \quad (27)$$

The plus or the minus sign in (27) should be adopted according as $\bar{c}$ is greater or less than $\bar{a}$. The values assumed for the various quantities occurring in (27) are given in Table XXI.

TABLE XXI

Maxwell Effect in Liquids

Liquid	$\delta_{\text{liq.}}$	T°C.	n_0	density	M	$\bar{a}$	$\bar{c}$	$\nabla \times 10^{12}$ calc.	$\nabla \times 10^{12}$ obs.
Heptyl alcohol	$2{\cdot}2 \times 10^{-3}$	20	1·425	0·8170	116·13	4·6	11·24	50·7	64
Octyl alcohol ..	,,	18	1·430	0·8276	130·14	,,	12·60	66·2	73
Heptylic acid ..	16×10^{-3}	20	1·423	0·9223	130·10	,,	11·24	112	527
Nonylic acid ..	,,	20	1·433	0·9070	158·14	,,	13·83	176	405

[1] See A. B. Rao, Proc. Ind. Acad. Sci., *5*, 124 (1937).

There is satisfactory agreement between the calculated and observed values in the two alcohols. The discrepancy in the case of acids suggests some further complication such as dipole association in these liquids. Recent work of Sadron[1] on the Maxwell effect in more complex substances such as polystyrenes and nitro-celluloses may also be referred to in this connection.

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[1] Jour. d. Phys., *8*, 481 (1937).

CHAPTER X

THE PRINCIPAL EXPERIMENTAL RESULTS IN RAMAN EFFECT

Raman Effect as an Outcome of the Earlier Work on Light Scattering.—In the preceding chapters of this book, an account is given of the subject in so far as it relates to that branch of the scattering of light which may be called the Rayleigh scattering. No change of wave-length is contemplated in this process and accordingly wave-lengths which are not present in the incident light are not expected to manifest themselves in the scattered light. While the subject was developing in the hands of Rayleigh, Born, Cabannes, Raman and others along the lines already outlined, suggestions were forthcoming from others that under certain circumstances, scattering of a different type, namely one in which a change of wave-length is involved, may be possible. While dealing with the subject of dispersion, Smekal[1] envisaged such a possibility. Kramers and Heisenberg[2] subsequently published a more detailed treatment of the quantum theory of dispersion and some aspects of this new type of scattered radiation were implicitly contained in their theory. The full significance of such implications was, however, realized only after the new radiations were experimentally discovered by Raman in 1928.

It seems proper to emphasize here that though the existence of the Raman effect may now be regarded as a vindication of the quantum theory of radiation and of the new mechanics, its discovery was quite independent of the latter and resulted as a natural sequel to the large amount of experimental work on the scattering of light carried on continuously at Calcutta by Raman and his co-workers since the year 1920. These investigations revealed at a very early stage the existence, in association with the Rayleigh type of scattering, of secondary radiations of

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[1] Naturwiss, *11*, 873 (1923).

[2] Z. f. Phys., *31*, 681 (1925).

altered wave-length. Certain characteristic features of these radiations, such as their persistence even after the most careful and repeated purification of liquids, have been established prior to the discovery itself. The true nature of the rays and particularly their spectral characters were, however, brought out only in the year 1928 by the use of spectrographs. The subject took an altogether new turn thereafter. Most of the main facts relating to the phenomenon, such as its presence in matter of all states of aggregation and its intimate relationship with the chemical nature of the scattering substance, were studied and described in the original paper by Raman which contained the announcement of the discovery itself.[1] About the same time, Landsberg and Mandelstam in Russia were also engaged in studying the scattering of light in crystals. They obtained similar results in quartz and these were published a few weeks later. The subject has since then been followed up in several laboratories with great vigour and the phenomenon has now come to be known as Raman effect. It is altogether distinct from Rayleigh scattering but is closely associated with it.

The following are the main events which led to the discovery of the Raman effect. The first observation of this feeble type of secondary radiation was made by Ramanathan[2] in 1923. He was led to it in attempting to explain why in certain liquids, the depolarization of the scattered light varied with the wave-length of the incident radiation. Let us imagine an arrangement, in which a particular filter is placed in the path of the incident beam and another which is complementary to the first is placed in the path of the scattered beam. In case there are no radiations of altered wave-length in the scattered beam, it is obvious that nothing will emerge out of the second filter. With the help of such complementary filters, Ramanathan detected the presence of a weak trace of light emerging out of the second filter in a number of cases. Even after exhaustive chemical purification and repeated slow distillation of the liquid in vacuum, the new radiations of altered wave-length persisted undiminished

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[1] Ind. Jour. Phys., *2*, 387 (1928).
[2] Proc. Ind. Assoc. Cult. Sci., *8*, 181 (1923).

in intensity showing that they were a characteristic property of the substance studied and were not due to any impurity. Krishnan[1] subsequently observed a similar effect in many other liquids. A somewhat more conspicuous phenomenon was then observed by Raman[2] in ice and in optical glasses. Venkateswaran then came across the strange case of glycerine, which showed this phenomenon in a striking manner. These radiations were also found to be strongly polarized, suggesting that their origin was distinct from the well-known fluorescence. The existence of a new phenomenon of a fundamental and distinct type was thus very clear and Raman, under whose direction all the work cited above was done, was firmly convinced that here was a case of light scattering which was somewhat analogous to the Compton effect. In a search for more powerful methods for the purpose of studying this effect, Raman first employed sun-light, concentrated by a powerful telescope, after passing it through filters having narrow regions of transmission. The results obtained clearly showed the urgent necessity for using a strictly monochromatic source for illuminating the substances and the mercury vapour lamp was soon hit upon. A spectrograph replaced the visual observation. The introduction of these two accessories, namely the mercury lamp and the spectrograph, may be regarded as a landmark in the history of the subject. He then made the startling observation that the spectrum of the scattered light from a variety of liquids and solids generally included a number of sharp lines or bands which were not present in the light of the mercury arc. The following are amongst the more important observations that were first made by Raman.

All the liquids examined (about 80 in number) showed the phenomenon in an unmistakable manner. The new type of radiation was also observed with special arrangements in a number of organic vapours and in gases like CO_2 and N_2O. Crystals like ice and certain amorphous bodies were examined and found to exhibit the effect. A spectrogram of the light

[1] Phil. Mag., *50*, 697 (1925).

[2] Jour. Opt. Soc. Amer., *15*, 185 (1927).

scattered by benzene was obtained with a small quartz spectrograph and sharp lines which were not present in the incident light were recorded. Several other liquids were visually examined and a similarity between the spectra exhibited by chemically similar liquids was noticed. The existence of a continuous spectrum in addition to the sharp lines in certain cases, the marked polarization exhibited by these lines and the less marked polarization exhibited by the continuous spectrum were observed and recorded.

These and other aspects of the subject were immediately followed up at Calcutta by a large number of workers. It has also found many adherents in other centres of research as the phenomenon proved to be of great theoretical interest. The discovery may be thus said to have opened up a new chapter in spectroscopy and furnished physicists and chemists with a very convenient and powerful tool of research into problems concerning the structure of matter. The main results obtained by these investigators will be outlined and discussed in the succeeding chapters of this book.

Nature of the Effect.—Reference has already been made to the universality of the Raman effect. The fact that it may be observed in a great variety of substances and in diverse physical states or conditions, and that the results are different in each different case make the field of investigation very extensive and bring it into relationship with many other branches of physical and chemical research. As actually observed, the effect consists in the appearance of new lines or in some cases bands and generally also some unresolved continuous radiation in the spectrum of the scattered light, besides the lines originally present in the incident radiation. Each line in the incident spectrum, if of sufficient intensity, gives rise to its own set of lines or bands and associated continuous spectrum. The frequency shifts are independent of the incident radiation and are therefore characteristic of the particular material studied.

It is noteworthy that the Raman lines generally show great differences in their intensity and in their width, some being sharp and others diffuse or even broad bands. It is an important property of the Raman radiations, observed in the transversely

scattered light, that they are often strongly polarized. The extent of such polarization, however, varies enormously for radiations of different frequency shifts and this is a very significant point to be considered in relation to their origin.

The continuous spectrum also shows great variations in intensity with different materials. It generally appears as wings extending slightly unsymmetrically on either side of the Rayleigh lines and shows little or no polarization. This is replaced by separate lines in gases in which it may be ascribed to the rotation of molecules. A continuous spectrum, having possibly a different origin, appears with very viscous liquids. It may sometimes be so strong as to overpower all the other lines. Some impure liquids also exhibit a continuous spectrum in the scattered light and a similar effect develops progressively in liquids that undergo chemical change under the action of light. The exact nature and origin of the continuous spectrum in each case are however not clear and different and conflicting views have been expressed in the literature.

Different Types of Raman Scattering.—When scattering of light with altered frequency occurs, we are evidently dealing with a case in which there is an exchange of energy between the quantum of radiation and the scattering particle according to the scheme

$$\text{Molecule} + h\nu \rightleftarrows \text{Molecule}^* + h\nu'.$$

The star on the right hand side indicates an excited condition of the molecule, the energy content in this case being more than that in the normal state. ν' is obviously less than ν. In the case of free molecules scattering light, one can distinguish between three different kinds of Raman effect, namely, an electronic effect, a vibrational effect and a rotational effect. The name in each case indicates the particular type of energy in the molecule which is added to or given up. Under certain circumstances, a mixed type, such as that obtained by superposing rotation on vibration, may also occur. The translational energy, in the case of free molecules, is, however, insignificant although it manifests itself, as we shall see later, in a conspicuous manner when it is present in the form of organized elastic waves, as in the case of a solid. Solids exhibit yet another type of Raman

effect in which the crystal lattice as a whole takes the place of the molecule in the above scheme. Different portions of the lattice while oscillating against each other are able to add to or take up energy from the incident quantum. Raman lines of this type are characteristic of only the solid state and are not present in liquids or gases. The above equation implies that the exchange of energy between the molecule and the incident quantum may be in either direction indifferently. In other words, we may have, in each of the above types of Raman effect, also an increase of frequency in scattering and not merely a decrease of frequency as in the Compton effect. We accordingly get the anti-Stokes and Stokes Raman lines or bands. The essential characters of the various types of Raman scattering may now be briefly enumerated.

Rasetti[1] observed a Raman line, which can be reliably classed as having an electronic origin, in the case of NO. The ground state of this molecule is double with a frequency interval of about 121 wave numbers per cm.[2] and a transition of the molecule from one sub-level to the other causes a Raman line as per the scheme,

$$\mathrm{NO}\ ({}^2\mathrm{P}_{\frac{1}{2}})+h\nu \rightleftarrows \mathrm{NO}({}^2\mathrm{P}_{\frac{3}{2}})+h\nu'$$

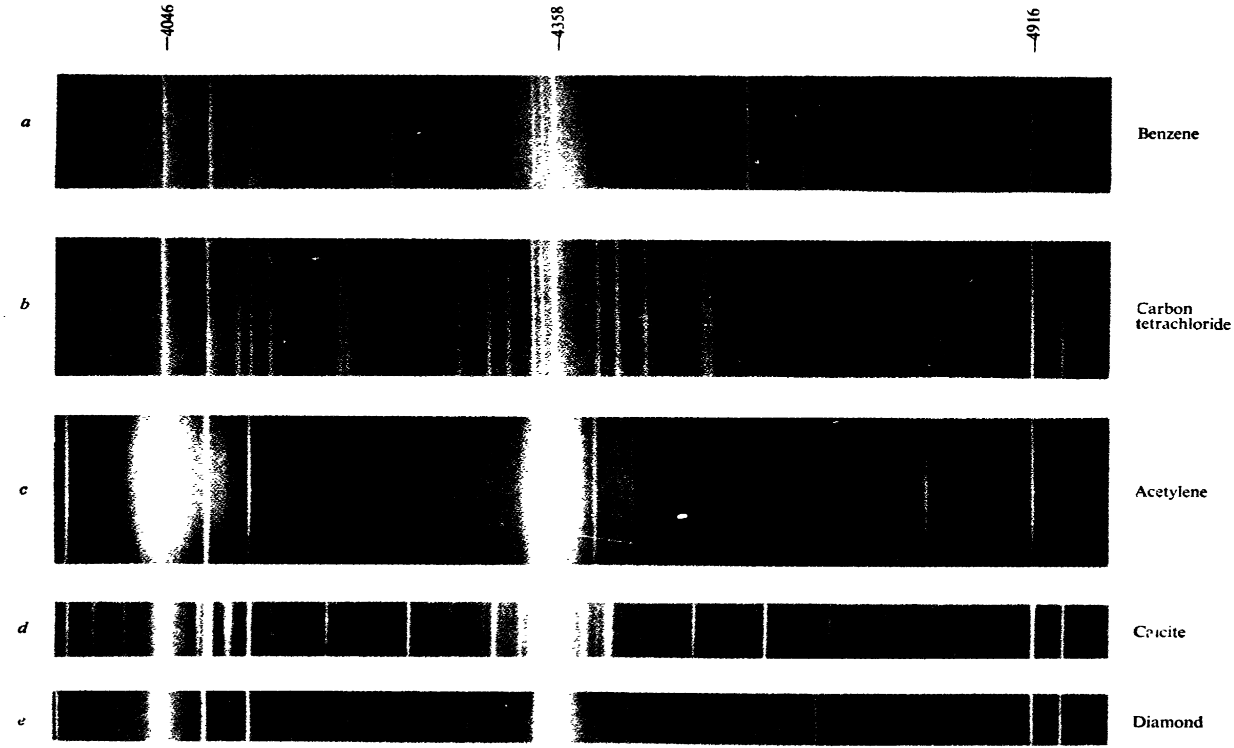
where $\nu = \nu' + 121$ cm.$^{-1}$

Most of the observed Raman lines with moderate or large frequency shifts have to be interpreted as due to a vibrational effect. A few typical Raman spectra obtained with benzene, carbon tetrachloride, acetylene, calcite and diamond are reproduced in Plate I. Numerous new lines and bands, exhibiting a variety of characters, are recorded and these are all to be regarded as vibrational Raman lines. The anti-Stokes lines are recorded with great intensity in carbon tetrachloride and calcite. Each one of the lines, recorded on the Stokes side, represents the capacity of the system to take up a certain quantity of energy and thus pass over into a state of vibrational excitation. We shall see later that most of these lines correspond to the various

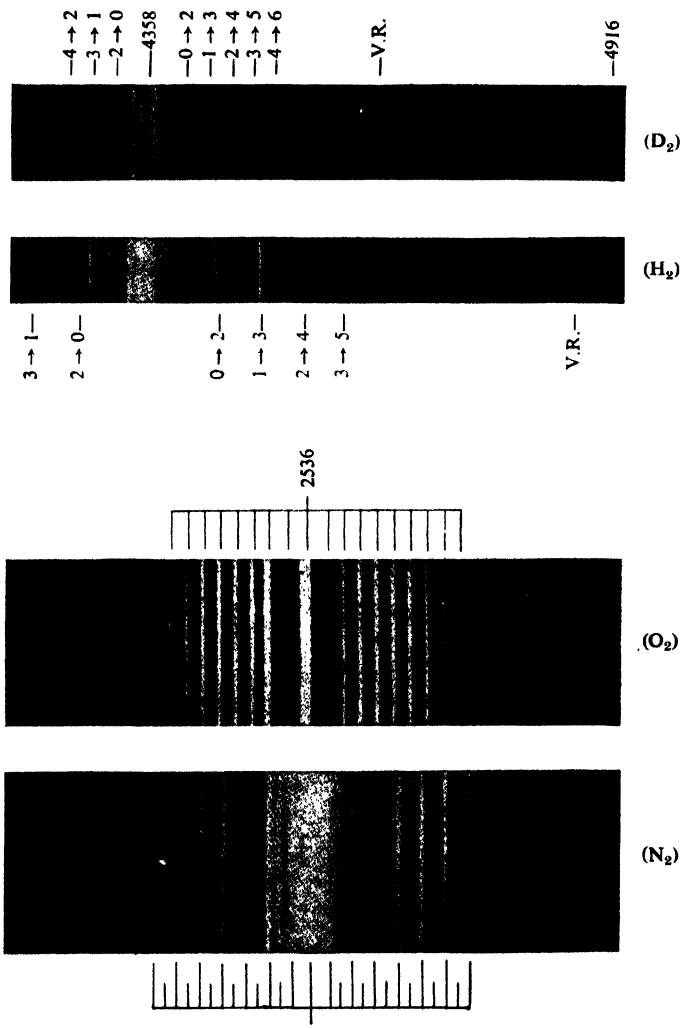
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[1] Phys. Rev., *34*, 548 (1929).

[2] Cm.$^{-1}$ will be used in future to indicate wave numbers per cm. Very often, this is also omitted for brevity and the numbers alone are given.



Raman Spectra



Raman Spectra of Gases

normal modes of oscillation of the molecule or the lattice as the case may be. Under certain favourable conditions, the possibility of the appearance of overtones and combination tones has also to be recognized and some of the fainter lines may have such an origin. There are also special cases where the overtones come out with considerable intensity in Raman scattering. Such cases are, however, only exceptions and are met with, much less frequently in Raman effect than in infra-red absorption.

The rotational Raman lines are obtained separately only in the case of molecules having a relatively small moment of inertia. Raman spectra of a few typical gases of this type, namely, D_2, H_2, O_2 and N_2 are reproduced in Plate II. In heavier gases, the lines are much closer and instruments of greater resolving power are needed to separate them. The general appearance of this type of Raman effect in such gases, when examined with a low dispersion instrument, is that of a continuous wing extending somewhat unsymmetrically on either side of the Rayleigh line. Using more powerful instruments, it has been found possible to resolve these patterns into separate lines in many cases. The alternation in the intensities of the individual lines, seen in H_2, D_2 and N_2, is a very significant result. O_2 is also of the same type but is to be regarded as an extreme case in which the alternate set of lines are of zero intensity. The pattern repeats itself in each case on the anti-Stokes side. In liquids[1], the situation appears to be somewhat different. In the close vicinity of the Rayleigh lines, a continuous spectrum (see *a* of Plate I) appears in the form of wings extending unsymmetrically on either side. This is most probably an unresolved rotational effect, the characteristic features of which are considerably modified by the close packing that is present in a liquid. In fact, the density of the liquid is so large that there is no justification to assume that the rotation of molecules will continue to be as free as in a gas. Accordingly, the pattern undergoes very striking alterations. In the solid state, these unresolved wings are replaced by broad bands. The

[1] Liquid hydrogen has so far been the only exception in that it gives separate rotational lines.

origin of these bands is not yet clear in all cases. They have, in certain cases, been identified with the internal oscillations of the crystalline lattice. Solid benzene is a case in which the intense continuous spectrum obtained in the liquid is replaced by bands in the solid. In calcite (see *d* of Plate I), two lines which are nearest to the exciting line may definitely be identified with the oscillations of the lattice, whereas the others are the usual vibrational Raman lines arising from the CO_3 groups. In this connection, the case of NaCl may be mentioned as it is of special interest. A Raman band, which is of very low intrinsic intensity, has been recorded and identified with an oscillation of the lattice. Diamond (see *e* of Plate I) is a remarkable case in that it exhibits a strong and sharp line possessing a comparatively large frequency shift which has to be ascribed to a lattice oscillation.

Significance of Raman Lines.—Quite apart from its various useful applications in physics and chemistry, the Raman effect possesses a unique interest with reference to the problem of the nature of radiation, the interaction of matter with radiation, and optical theories generally. In the Compton effect, we have the case of an electron weakly bound to an atomic nucleus acquiring momentum and being freed from the atom as the result of its scattering a quantum of radiation; the nucleus plays a minor part in the process. In the Raman effect, on the other hand, we are dealing with a very general case of interaction between the quantum of radiation and matter; the latter may be the molecule of a gas or even a molecular aggregate such as a liquid or a crystal. The relationship between the two effects becomes clearer, if we limit ourselves to a case in which the scattering particle is a single molecule which undergoes only a change in its electronic energy. We then have an electronic Raman effect, which becomes identical with the Compton effect if the electron is actually dislodged and rendered free, but differs from it if the electron remains bound to the molecule in a higher level of energy.

The complete analysis of the vibrational Raman spectrum of any molecule, when taken in conjunction with the infra-red data, throws considerable light on its structure. Numerous

cases of special significance have been studied in the recent years and the vast subject of molecular oscillations in relation to Raman spectra is dealt with in a later chapter.

The rotational Raman lines of certain simple molecules like H_2, D_2, N_2, O_2, CO_2 and N_2O have brought to light the ultimate structure of these molecules in a remarkable manner. The early work of McLennan and McLeod[1] on liquid hydrogen may be specially mentioned in this connection. Their observation of the alternation in the intensities of the rotational lines furnished an experimental proof of the existence of two forms of hydrogen. As is well known, this result was previously anticipated by the theoretical investigations of Heisenberg and was supported by Dennison's discussion of the data for the specific heat of hydrogen. Similar results were obtained by Rasetti[2] and by Bhagavantam[3] in the case of the hydrogen gas. The striking experiments of McLennan, Smith and Wilhelm[4] have subsequently shown that the slow transformation of one form of hydrogen to the other form, at liquid hydrogen temperatures, can be studied by following the changes in the intensity of the lines in the Raman spectra over a sufficiently long period of time. The observed intensities[5] and the fact that the system of Raman lines coming from molecules characterized by odd rotational quantum numbers is the stronger of the two sets have furnished the results that the hydrogen nucleus has a spin moment of half a unit, conforms to Fermi-Dirac statistics and that the statistical weight of the odd rotational levels is three times that of the even rotational levels. These results are in entire agreement with what we know of the hydrogen nucleus from other branches of physics. The next simple molecule studied is D_2 and the preliminary work of Anderson and Yost[6] followed by the work of Teal and MacWood[7] and a quantitative study of the intensity

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[1] Nature, *123*, 160 (1929). [2] Phys. Rev., *34*, 367 (1929).

[3] Ind. Jour. Phys., *7*, 107 (1932).

[4] Trans. Roy. Soc. Canada, *23*, 247 (1929).

[5] A detailed comparison of the observed intensities with the theory is made in a later chapter.

[6] Jour. Chem. Phys., *3*, 242 (1935).

[7] *Ibid.*, *3*, 760 (1935).

relationships amongst the various Raman lines by Bhagavantam[1] has led to several important results in this case also. Raman lines coming from transitions between even levels are stronger than those representing transitions between odd levels and this, coupled with the actual distribution of intensities, leads to the results that the deuterium nucleus has a spin moment of one unit, conforms to Bose-Einstein statistics and that the statistical weight of the even rotational levels is two times that of the odd rotational levels. In all these respects, the nucleus differs from the hydrogen nucleus and the results are in complete accordance with those derived from other branches of physics.

Rasetti obtained the rotational effect in oxygen and nitrogen. His pictures are reproduced in Plate II. In the case of the former gas, the entire rotational spectrum consists of only alternate (odd) levels and the results are in perfect agreement with band spectrum data and with what may be expected theoretically in the absence of a nuclear spin. In nitrogen, however, we have an alternation of intensities, the transitions between even rotational levels giving rise to lines of greater intensity. This is quite unlike the case of hydrogen but similar to that obtained in deuterium. We have therefore to conclude that the nitrogen nucleus conforms to Bose-Einstein statistics. The relative intensities of the two sets of lines may be accounted for satisfactorily, if we ascribe a spin moment of one unit to the nitrogen nucleus as is the case with deuterium. These results in respect of the nitrogen nucleus were first revealed from a study of the Raman spectra.

Amongst the polyatomic molecules, the cases of CO_2 and N_2O are of interest. The rotational Raman spectrum of the former consists only of alternate (odd) levels like O_2 and it therefore should be regarded as having a symmetrical structure. N_2O has been shown to give both sets of rotational Raman lines without any alternation in intensities, a result which is of considerable importance as it leads to an unsymmetrical structure for N_2O. Such an unsymmetrical structure is also confirmed from an analysis of the vibrational Raman spectrum in relation

[1] Proc. Ind. Acad. Sci., *2*, 303, 310 and 477 (1935).

to its infra-red absorption. Heteronuclear molecules like HCl, NO, CO and HD have been studied and found to give rotational Raman spectra in which the phenomenon of alternating intensities is absent. This is in accordance with what we should expect. It has already been remarked that in the place of separate rotational lines, we get unresolved wings in relatively complicated molecules. These wings are found to exhibit great variations in intensity from substance to substance. These variations can be correlated with the variations of the optical anisotropy of the molecules; molecules which are highly anisotropic like benzene showing the effect strongly and those which are spherically symmetrical like CCl_4 showing it to an extent hardly appreciable. In fact, in a later chapter we shall see that the intensity of the rotational Raman scattering primarily depends upon the optical anisotropy of the molecule.

The existence of anti-Stokes Raman lines is also of great significance. The ratio of the intensities of the radiations of diminished and increased frequencies should nearly be the same as the ratio of the populations of normal and thermally excited molecules. The latter ratio may be derived with the help of the Boltzmann theorem. This may justly be regarded as a proof of the real existence of discrete stationary states and of the perfect reversibility of the interaction between radiation and matter. The fact that the experimentally observed intensity ratios agree with those predicted on the basis of the Boltzmann formula may further be taken as a proof of the correctness of the Boltzmann theorem.

Relationship to Infra-red Absorption.—From what has been said in the foregoing pages, it is clear that the rotational and vibrational Raman spectra will bear a close resemblance to the far infra-red and the near infra-red absorption spectra of molecules respectively. The latter arise from a direct absorption of energy which takes place only when the incident light is of the appropriate frequency whereas the former arise by a similar but distinctly different process in which the appropriate fraction of energy is absorbed from the incident light quantum, whatever the frequency of the latter may be. The ultimate result, as far as the molecule is concerned, is the same in both cases but the

selection rules that govern the two phenomena are quite different. The selection rules that govern the appearance of Raman lines will be discussed in greater detail in a following chapter but they may be briefly stated here as follows. The selection rules in respect of infra-red absorption are also cited for comparison. A rotational Raman line, due to exchange of rotational energy between a molecule and an incident light quantum, occurs only when the molecule involved is optically anisotropic. The greater the optical anisotropy, the greater is the intensity of this type of scattering. The corresponding condition, necessary for the occurrence of pure rotational or far infra-red absorption, is the presence of a permanent dipole in the rotating molecule. A vibrational Raman line, due to exchange of vibrational energy between a molecule and an incident light quantum, occurs when the mode of oscillation involved causes either a change in the mean polarizability of the molecule or a change in the individual values of the principal components of the polarizability ellipsoid or both. The greater this change, the greater is the intensity of this type of scattering. The corresponding condition, necessary for the occurrence of vibrational or near infra-red absorption, is that the mean electric moment of the molecule should undergo a change when the molecule oscillates, for the particular oscillation in question.

It is thus clear that all electrically non-polar but optically anisotropic molecules like H_2, O_2, N_2, etc., will give rise to pure rotational Raman spectra but will not give rise to any far infra-red absorption. On the other hand, symmetric oscillations[1], such as those that occur in CO_2, CS_2, NO_3^-, etc., cause no change in the electric moment and hence cause no infra-red absorption. They, however, cause a large variation in the mean refractivity and hence give rise to intense vibrational Raman lines. It is thus obvious that sometimes lines which do not appear in the infra-red absorption may appear strongly in the Raman effect and

[1] In CO_2 and CS_2, this oscillation consists of a symmetrical movement of the two outer atoms along the valency bonds. In the nitrate ion, the symmetric oscillation is one in which all the oxygen atoms move radially, nitrogen remaining fixed at the centre.

vice versa. In such cases, a study of the Raman effect provides a picture that is complementary to that provided by infra-red absorption.

Correlation between the infra-red and the Raman spectra for two simple molecules, namely CO_2 and CS_2, is shown in Table XXII. The case of nitrate and carbonate ions is similarly dealt with in Table XXIII.

TABLE XXII

Normal Frequencies of CO_2 and CS_2

Frequency	Mode	CO_2	CS_2	Active in [1]
A_{1g} (ν_1) ..		1388	655	Raman effect.
E_{1u} (ν_2) ..		668	397	Infra-red.
A_{1u} (ν_3) ..		2363	1523	Infra-red.

TABLE XXIII

Normal Frequencies of NO_3 and CO_3

Frequency	Mode	CO_3^{-}	NO_3	Active in [2]
A_1' (ν_1) ..	Total symmetric ..	1088	1050	Raman effect.
A_2'' (ν_2) ..	Transverse to plane	880	830	Infra-red.
E_1' (ν_3) ..	Degenerate, in the plane.	1438	1360	Raman effect and Infra-red.
E_1' (ν_4) ..	Do. ..	714	720	Do.

ν_1 of CO_2 and CS_2 appears only in Raman effect and is not present in infra-red absorption. Similar remarks hold good in respect of ν_1 in CO_3^{-} and NO_3^{-}. The reverse is the case for ν_2 and ν_3 in CO_2 and CS_2 and ν_2 in CO_3^{-} and NO_3^{-}. It may be mentioned here that the Raman spectra of these substances contain more lines than are indicated in Tables XXII and XXIII but these have been satisfactorily explained as due to special causes.

[1] This relates to only the fundamentals. It does not imply that the overtones will be subject to the same selection rules.

A close examination of the infra-red absorption spectrum and the Raman spectrum of benzene shows that none of the Raman lines are represented in infra-red absorption and *vice versa*. In view of the great importance of this result, we shall deal with it here in some detail. Table XXIV contains a correlation of the two spectra for benzene.[1] Raman frequencies given in bold type are either strong or medium intensity lines and have been recorded by almost all the investigators. Those given in ordinary type are weak lines but the existence of these has been established beyond any doubt. The frequencies given in italics are very weak and have mostly been recorded by one or two observers only. Similar remarks apply to the infra-red frequencies also. A few more components have been recorded on either side of the principal Raman line 992 but these are not included in the Table. Frequencies in respect of which there is a possibility of coincidence between the Raman values and the infra-red values, either in the vapour or the liquid state or both, are entered one below the other. These coincidences are most probably only accidental and have no real significance. Owing to deformation arising from close packing in the liquid state, certain apparent coincidences may arise and these may be classified as (*a*) strong Raman frequencies appearing either weakly or strongly in the liquid absorption but not at all in the absorption by vapour, (*b*) strong infra-red frequencies appearing only weakly in the Raman spectrum, (*c*) frequencies which should not occur in either the Raman or the infra-red spectra but occur only weakly in Raman spectra and perhaps strongly in the liquid absorption and not at all in the vapour absorption. With this classification in view, we may easily see that coincidences 1, 5, 7, 9, 13 and 14 belong to class (*a*). The absorption at 1617 in the vapour is distinct and is not to be regarded as a coincidence with either component of the typical doublet 13 and 14. Coincidences 8 and 12 are of the class (*b*) and 3, 10 and 16 belong to class (*c*). Coincidences 2, 6 and 11 are rejected as the differences are well beyond experimental errors. 17 is also

[1] The values quoted here are taken from a series of papers published by Angus and others in the Journal of the Chemical Society (1936).

not a real coincidence and it is suggested that 18 is most probably a coincidence of type (*a*) in which case 3080 in the vapour

TABLE XXIV

Infra-red and Raman Spectra of Benzene

Raman lines ..	404	(1) **605·6**	(2) 685	(3) *781* (4) *802*	*824*	(5) **848·9**	(6) *992* satellite	(7) **991·6**	(8) 1030
Infra-red maxima in vapour ..	..	..	**671**	*793*	..	..	*962*	..	**1037**
Infra-red maxima in liquid ..	..	610	**671**	**773**	..	**849**	..	985	**1033**
Raman lines ..	..	(9) **1178**	..	(10) *1285*	*1326*	(11) 1404	*1449*	(12) 1478	..
Infra-red maxima in vapour ..	*1143*	..	*1240*	..	..	1377	..	**1485**	..
Infra-red maxima in liquid ..	..	**1170**	..	1298	..	**1381**	..	**1480**	1529
Raman lines ..	(13) **1584·8**	..	(14) **1606·4**	..	1693	..	*1827*	..	*1936*
Infra-red maxima in vapour ..	..	1617	..	..	..	**1808**	..	*1906*	..
Infra-red maxima in liquid ..	**1584**	..	**1604**	**1669**	..	**1810**	..	..	..
Raman lines ..	..	*1988*	*2030*	*2128*	..	(15) 2293	(16) *2358*	2454	2543
Infra-red maxima in vapour ..	**1965**	.	..	..	..	2288	..	..	..
Infra-red maxima in liquid ..	**1963**	..	..	..	2223	..	2356	..	..
Raman lines ..	2618	..	*2688*	..	2925	2948	(17) **3046·8**	(18) **3061·9**	*3164*
Infra-red maxima in vapour ..	..	..	..	*2857*	..	.	..	**3080**	
Infra-red maxima in liquid ..	..	2629	..	..	..	..	extension of 3070	**3070**	..
Raman lines ..	3187	*3467*	..	*3680*	..	*3916*	..	..	..
Infra-red maxima in vapour ..	..	..	..	..	..	..	..	..	..
Infra-red maxima in liquid ..	..	..	*3655*	..	*3700*	..	*4060*	*4604*	*5984*

absorption has to be regarded as distinct from 3062 of the Raman spectrum. We are now left with 4 and 15 which have little importance, as the frequencies in both cases are weak. The agreement, particularly in 4, is not very good. Thus we arrive at the conclusion that there is no case of a genuine coincidence between the infra-red and Raman frequencies. Further support to this contention has been made available by Angus and others who have extended the investigations to hexa-deuterobenzene as well. This result is of great significance in relation to the structure of the benzene molecule and we shall have occasion to refer to it again.

For an unsymmetrical molecule like acetic acid, there are a large number of coincidences as may be seen from the data given in Table XXV.

TABLE XXV

Infra-red and Raman Spectra of Acetic acid

Raman lines ..	443	603	621	869	893	942	1014	1221	1276
Infra-red maxima ..	..	..	..	870	893	935	1010	1227	..
Raman lines ..	1370	1431	1667	1726	1771	2943	2996	3033	..
Infra-red maxima ..	1389	..	..	1706	..	..	..	..	..

Intensity and Polarization Characters of Raman Lines.—In spite of the numerous experimental difficulties in the way of an accurate study of these features, results of fundamental and far-reaching importance have been obtained. Very faint Raman lines and bands as well as very intense ones are met with. Some illustrations of the former are the band in NaCl recorded by Rasetti[1] and the anti-Stokes Raman line in diamond recorded by Bhagavantam.[2] The principal Raman line of diamond at 1332 and the one having a frequency shift of 992

[1] *The Structure of Molecules, Leipziger Vortrage* (Eng. Trans.), 55 (1932).
[2] Ind. Jour. Phys., *5*, 573 (1930).

in benzene may be cited as examples of very intense Raman lines. These may be recorded in a very short time with reasonably powerful instruments. The intensity of a Raman line, when expressed as a fraction of the parent Rayleigh line, is usually a few hundredths in liquids and a few thousandths in gases.[1] Reliable data in this direction are, however, available only in a few cases. These extra ordinary variations in intensity as we pass from substance to substance and from line to line are of great significance and have provided the clue to the unravelling of many minor problems relating to molecular structure. For instance, we get the vibrational Raman line in HCl gas and liquid but not in an aqueous solution of HCl which presumably consists of hydrogen and chlorine ions. In aqueous solutions of salts, where ionization is complete, we find no Raman lines characteristic of the salt as a whole but only those corresponding to the molecules of water and the separated ions. Most of the organic substances and certain metallic halides such as the mercurous and mercuric chlorides which are known to

TABLE XXVI

Intensity and Polarization of Raman lines in CCl_4

Frequency	$\frac{I_{\text{Raman}}}{I_{\text{Rayleigh}}} \times 10^3$				Depolarization
	Daure[2]	Carrelli and Went[3]	Dhar[4]	Veerabhadra Rao[5]	
217	10	18	1·9	3·0	0·86
315	13	22	3·4	3·6	0·86
459	6	16	3·0	2·5	< 0·05
762 } 792 }	7·5	6	1·2	{ 0·8 { 0·8	0·86

[1] Hydrogen and deuterium are exceptions to this statement. In these cases, the Raman line is only a few hundredths of the Rayleigh line.

[2] Ann. d. Phys., *12*, 375 (1929).

[3] Z. f. Phys., *76*, 236 (1932).

[4] Ind. Jour. Phys., *9*, 189 (1934).

[5] Z. f. Phys., *97*, 154 (1935).

be covalent compounds, exhibit strong Raman lines. From these and other results, Krishnamurti concluded that the intensity of a Raman line depends very much on the chemical nature of the linkages in the molecule, being very low in electrovalent compounds and very high in covalent compounds. Results regarding the intensities of Raman lines in a few typical liquids are given below.

TABLE XXVII

Intensity and Polarization of Raman lines in Benzene

Frequency	$\frac{I_{\text{Raman}}}{I_{\text{Rayleigh}}} \times 10^3$				Depolarization
	Daure	Carrelli and Went	Dhar	Veerabhadra Rao	
605	..	1·28	3·5	0·44	0·86
851	..	0·93	1·9	0·21	..
992	5·0	10·9	9·5	4·20	< 0·05
1181	1·5	2·4	4·5	0·50	0·86
1586 } 1608 }	2·5	1·8	3·8	0·25 / 0·14	0·86 / 0·86
3046 } 3063 }	7·0	6·6	..	1·23 / 1·57	0·86 / 0·30

TABLE XXVIII

Intensity and Polarization of Raman lines in Chloroform

Frequency	$\frac{I_{\text{Raman}}}{I_{\text{Rayleigh}}} \times 10^3$		Depolarization
	Dhar	Veerabhadra Rao	
261	5·4	2·50	0·86
366	4·0	1·90	0·18
667	2·4	2·10	0·06
759	1·7	0·49	0·86
1213	..	0·31	0·86
3020	..	0·67	0·25

Figures, given by various authors for the intensities, differ very widely and hence no attempt is made to strike a mean. In this connection, a recent paper by Veerabhadra Rao[1] in which attention is drawn to the various errors that are involved in such determinations, is of considerable interest. The figures may be regarded as giving only the order of magnitude. The discrepancies in respect of the depolarization values are not so prominent and hence either a mean of the values obtained by various investigators or the most probable value is given in the Tables.

Closely connected with this issue is the question of the state of polarization of the Raman lines. Just as we meet with Raman lines having a great variety of intensities, we also meet with lines having a wide range of polarization characters. The study of polarization has taken two different courses, namely the use of incident unpolarized light and the use of incident circularly polarized light. In the former case, the depolarization factor or the ratio of the horizontal to the vertical component is expressed for each Raman line and is found to vary between 0 and 0·86 for the vibrational lines. The rotational Raman lines have always a depolarization factor of 0·86. A few typical results in respect of the vibrational lines in liquids are given in Tables XXVI to XXVIII. Table XXIX contains the few results that are available in respect of the vibrational lines in gases.

TABLE XXIX

Depolarization of the Vibrational Lines in Gases

Gas ..	H_2	D_2	N_2	O_2	CO_2	C_2H_2	CO	NO	NO_2		NH_3
Frequency ..	4156	2993	2331	1557	1389	1974	2143	1876	1285	2223	3335
Depolarization ..	0·13[2]	0·18[2]	..	..	0·20[2]	0·2[2]	..	..	..	..	..
	0·045[3]	..	0·19[3]	0·26[3]	0·21[3]	..	0·29[3]	0·31[3]	0·22[3]	0·38[3]	0·12[3]

Experiments with incident circularly polarized light have first been initiated by Bär[4] and by Hanle[5] and these have

[1] Proc. Ind. Acad. Sci., 7, 208 (1938).

[2] Bhagavantam, Ind. Jour. Phys., *6*, 319 (1931).

[3] Cabannes and Rousset, Comptes Rendus, *202*, 1825 (1936).

[4] Helv. Phys. Act., *4*, 130 (1931).

[5] Naturwiss., *19*, 375 (1931).

yielded very interesting results. Observations are made either in the forward or backward direction and part of the line is found to be reversely circularly polarized and the other part circularly polarized in a sense similar to that of the incident light. The ratio of the former to the latter, which may be denoted by P, is called the reversal factor and is determined for each line. This is found to vary between 0 and 6. In fact, it will be shown later that the reversal factor is given by $\rho/1-\rho$ for any Raman line having a depolarization factor of ρ. This relationship has been verified by Hanle in a number of cases. It is easily seen that for $\rho < \frac{1}{2}$, the reversal factor is less than unity and such a Raman line will therefore exhibit normal circular polarization. Lines having $\rho = \frac{1}{2}$ will have $P = 1$ and will therefore be unpolarized. Lines having $\rho > \frac{1}{2}$ will have their reversal factors greater than one and will therefore be reversly circularly polarized. Highly depolarized lines such as the rotational Raman lines should thus exhibit reverse circular polarization. These conclusions have been verified in a large number of cases. Results obtained by Bär[1] in a typical case are given in Table XXX. Subsequently, Heidenreich[2] quantitatively connected the reversal factors with the depolarization factors in a number of cases.

TABLE XXX

Relation Between Depolarization and Reversal Factors in Benzaldehyde

Frequency	I	$\rho \times 100$	Circular Polarization
139	2	86	Strongly reversed.
239	1*b*	87	,, ,,
439	4	33	,, positive.
615	3	89	,, reversed.
648	1	0	Positive.
827	3	7	Strongly positive.
1001	8	7	,, ,,
1164	5	63	Weakly positive.
1203	6	35	Positive.
1597	10	88	Weakly reversed.
1700	7	42	,, positive.
3063	5*b*	35	,, ,,

[1] Z. f. Phys., *79*, 455 (1932). [2] *Ibid.*, *97*, 277 (1935).

Amongst the other significant results, mention may be made of the fact that a high intensity and sharpness of a Raman line are usually accompanied by a low depolarization factor, while a low intensity and diffuseness are usually accompanied by a high depolarization factor. Corresponding lines in molecules having like structures have nearly the same depolarization factors. This is well illustrated by the cases of chloroform and bromoform. The results are given below. Figures in the brackets represent the depolarization factors.

$CHCl_3$: 261(0·86) 366(0·18) 667(0·06) 759(0·86) 1213(0·86) 3020(0·25)
$CHBr_3$: 154(0·86) 222(0·20) 538(0·05) 654(0·86) 1146(0·86) 3023(0·22)

This is what we should expect, as the polarization of a Raman line is mainly decided by the symmetry of the oscillation.

Breadth and Fine Structure of Raman Lines.—Numerous attempts have been made, since the discovery of the Raman effect, to study the characters of both Rayleigh and Raman lines under high dispersion and a considerable amount of work yet remains to be done. The subject may be divided into two parts, namely the fine structure and breadth of the Rayleigh lines including the accompanying rotational effect or the wings and the fine structure and breadth of vibrational Raman lines. A great deal of work has been done by Gross[1] and others and more recently by Raman and his co-workers[2] on the fine structure of the Rayleigh line in liquids. Besides the undisplaced line, two components which are very close to the centre (about 0·3 $cm.^{-1}$ on either side) have been detected. The presence of these two components may be explained by considering the existence of sound waves in the liquid which scatter the incident light in accordance with the Einstein-Brillouin theory. Their positions and the effect on the same of changing the frequency of the incident radiation or the angle of observation are in agreement with what may be expected on the basis of the above theory. The appearance of the central component is, however, not contemplated in this theory and should not be

[1] Z. f. Phys., *63*, 685 (1930) and Nature, *126*, 201, 400 and 603 (1930).

[2] See numerous papers in the Proceedings of the Indian Academy of Sciences.

expected in a solid. Its presence in the liquid only indicates that not all of the thermal energy of the molecules is organized in the form of sound waves but that some of it is akin to the random type that occurs in gases. Amongst other interesting results that have been obtained in this direction, the following may be mentioned. All the three components are found to exhibit a very high degree of polarization. Their relative intensities differ from liquid to liquid, the central component being particularly bright in certain liquids such as CCl_4. Variations in their relative intensities and other characters occur with changing temperature.

Closely associated with these results are the facts regarding the distribution of intensity in the wings accompanying the Rayleigh line. Studies under high dispersion have shown that the continuous wing cannot be separated from the centre and that it starts with a maximum intensity at or very near the centre.

In the case of vibrational Raman lines, the results relating to breadth and fine structure are more numerous and varied. In the case of gases, broad lines or bands are somewhat unusual whereas they are met with quite frequently in liquids. The reason for the breadth or the fine structure of a vibrational Raman line may be any one of the following, namely, (i) an unresolved rotational Raman spectrum accompanying the vibrational line, (ii) closely spaced components arising from the fact that molecules having different rotational energies have slightly different vibrational frequencies, (iii) closely spaced components arising from the fact that molecules in different states of vibrational excitation may give rise to slightly different vibrational frequencies, (iv) components arising from isotropic molecules, (v) a broadening due to the existence of polarity and close packing as in liquids composed of polar molecules, etc. Any one of these causes or some of them operating together may result in a broad line. The two bands at 650 and 687 in acetylene gas, the fine structure of the vibrational line in hydrogen, the principal Raman line at 650 in carbon disulphide and its satellite, the principal Raman line at 992 in benzene and its satellite or 450 in CCl_4 and its satellites and the bands of

water may be cited as examples in which causes i, ii, iii, iv and v are respectively operative. This variety of causes and a fascinating series of results obtained in each case have to be dealt with in greater detail in order to bring out their full significance.

CHAPTER XI

THEORY OF RAMAN SCATTERING

Preliminary Considerations.—It has already been mentioned that a Raman line may, in a general manner, be regarded as the result of an impinging light quantum of frequency ν exchanging energy with a molecule in accordance with the following scheme.

$$\text{Molecule} + h\nu \rightleftarrows \text{Molecule}^* + h\nu'$$

The incident light quantum is re-emitted as one of altered frequency ν'. *Prima facie*, the exchange of energy may be either way. The molecule may gain in energy, the emitted light then having a lower frequency than the incident light (Stokes Raman lines). The molecule which is intially in an excited state may lose energy, the emitted light then having a higher frequency than the incident light (anti-Stokes Raman lines). It is clear that in either case, only certain discrete values of energy will be exchanged, these quantities being characteristic of the molecule. Any theory of the Raman effect should therefore concern itself with investigating the mechanism of such an exchange and the conditions under which and the probability with which such an exchange takes place. We shall, in the first instance, give an elementary treatment of the subject.

The general principles, on which the theory of molecular scattering is based, are that an incident electric field $E_0 \sin 2\pi\nu_0 t$ induces an oscillating electric moment $\alpha E_0 \sin 2\pi\nu_0 t$ in the molecule. The molecule then behaves as a Hertzian oscillator and radiates energy in the form of electromagnetic waves of frequency ν_0. The laws of intensity and polarization are the same as those of a Hertzian oscillator and have been derived in an earlier chapter. If we now imagine some kind of a mechanism intrinsic in the molecule itself by which the amplitude of the emitted wave is altered periodically with a frequency ν, it is obvious that the electric moment of the oscillator at any given instant is represented by the expression

$$\alpha\, E_0 \sin 2\pi\nu_0 t \cos (2\pi\nu t + \varepsilon),$$

which may be written as

$$\tfrac{1}{2}\alpha E_0 \left[\sin\{2\pi(\nu_0+\nu)t+\varepsilon\}+\sin\{2\pi(\nu_0-\nu)t-\varepsilon\}\right].$$

This expression shows that the emitted light will consist of two frequencies $\nu_0+\nu$ and $\nu_0-\nu$. If any part of the induced moment is not subject to this periodicity, we then obtain the incident frequency ν_0 also in the emitted light. Thus in a general case, the emitted light will consist of frequencies ν_0 and $\nu_0 \pm \nu$ when the incident light is of frequency ν_0.

Periodicity Introduced by an Oscillating Molecule.—Let us take a diatomic molecule whose vibration frequency is ν. If the mean polarizability α of the molecule is a function of the nuclear distance, it is easily seen that α will undergo periodic variations, when the molecule is oscillating. At any instant, the mean polarizability may be represented by $\alpha_0+\left(\frac{d\alpha}{dr}\right)_0 \sigma \cos(2\pi\nu t+\varepsilon)$, where σ is the amplitude or the maximum value of $\triangle r$. ε represents the phase of the molecular oscillation whose value is arbitrary. α_0 is the polarizability of the molecule in the equilibrium position. The induced moment may be written as

$$E_0 \sin 2\pi\nu_0 t\left[\alpha_0+\left(\frac{d\alpha}{dr}\right)_0 \sigma\,(\cos 2\pi\nu t+\varepsilon)\right].$$

The above expression may be split up into three terms and written as

$$\alpha_0 E_0 \sin 2\pi\nu_0 t+\left(\frac{d\alpha}{dr}\right)_0 \sigma\frac{E_0}{2}\Big[\sin\{2\pi(\nu_0+\nu)t+\varepsilon\}$$
$$+\sin\{2\pi(\nu_0-\nu)t-\varepsilon\}\Big].$$

The first term gives rise to Rayleigh scattering, the frequency being ν_0. The intensity of scattering per molecule is proportional to α_0^2, in case the incident electric vector is one unit. The second and third terms give rise to Raman lines of frequencies $\nu_0+\nu$ (anti-Stokes) and $\nu_0-\nu$ (Stokes) respectively, their intensities per molecule per unit incident electric vector being proportional to

$$\frac{\sigma^2}{4}\left(\frac{d\alpha}{dr}\right)_0^2.$$

Owing to the presence of a phase factor ε, which varies arbitrarily from molecule to molecule, different molecules will act as independent sources of radiation. The total intensity from n molecules will be simply n times that obtained from a single molecule.[1]

When we are interested in the inter-comparison of the Stokes and anti-Stokes Raman lines, besides the factor noted above, we also have to take into account the fact that the intensity of the light emitted by an oscillating dipole is inversely proportional to the fourth power of the emitted wave-length. This gets absorbed into the constant of proportionality, if we are comparing beams of the same wave-length but in a case like that of Stokes versus anti-Stokes, it has to be explicitly taken account of, as their wave-lengths are different. For instance, the intensity of the Raman line of frequency $\nu_0+\nu$ will be proportional to $\frac{\sigma^2}{4}\left(\frac{d\alpha}{dr}\right)_0^2(\nu_0+\nu)^4$ whereas that of the line of frequency $\nu_0-\nu$ will be proportional to $\frac{\sigma^2}{4}\left(\frac{d\alpha}{dr}\right)_0^2(\nu_0-\nu)^4$. This fourth power factor will, however, be omitted in the following paragraphs for brevity but the necessity for taking it into account should be clearly borne in mind. The above expression may be put in a slightly different form, if we assume that the energy of the oscillator, which is given by $2\pi^2\nu^2\mu\sigma^2$, is equal to $h\nu$ thus giving

$$\sigma^2 = \frac{h}{2\pi^2\nu\mu}.$$

μ is the reduced mass and after introducing the letter B for $h/8\pi^2\mu r_0^2$, we can easily see that the intensity is proportional to[2]

[1] Unlike the case of Rayleigh scattering, increased density of the medium does not affect this result. In the case of Rayleigh scattering, the lack of correlation between the individual phases depends on the lack of correlation between the positions of the molecules. The result is accordingly considerably affected by the nature of aggregation. On the other hand, Raman scattering is incoherent under all circumstances as this property is obtained quite independently of the nature of aggregation.

[2] α' and γ' here have a significance different from that already ascribed to them in the earlier chapters.

$$\frac{B}{\nu} r_0^2 \left(\frac{d\alpha}{dr}\right)_0^2 \text{ or } \frac{B}{\nu}\alpha'^2, \text{ where } \alpha' = r_0\left(\frac{d\alpha}{dr}\right)_0.$$

In the case of an anisotropic molecule, we have already seen that the parallel component of Rayleigh scattering is proportional to $\alpha_0^2+\frac{4}{45}\gamma_0^2$ and $\alpha_0^2+\frac{7}{45}\gamma_0^2$, according as we use plane polarized or unpolarized incident light. A slight extension of the above reasoning will easily show that the corresponding expressions for the Raman lines will be $\frac{B}{\nu}(\alpha'^2+\frac{4}{45}\gamma'^2)$ and $\frac{B}{\nu}(\alpha'^2+\frac{7}{45}\gamma'^2)$. The perpendicular components in the two cases will respectively be $\frac{B}{\nu}\cdot\frac{3}{45}\gamma'^2$ and $\frac{B}{\nu}\cdot\frac{6}{45}\gamma'^2$.

Periodicity Introduced by a Rotating Molecule.—The periodic variation of the induced moment may also be effected by the rotation of an anisotropic molecule with reference to the incident light vector. We shall take the very simple case of a diatomic molecule rotating about an axis OX′ (θ, φ) lying in the symmetry plane X′ Y′ (A=B), the incident light vector being parallel to the Z axis (Fig. 19).

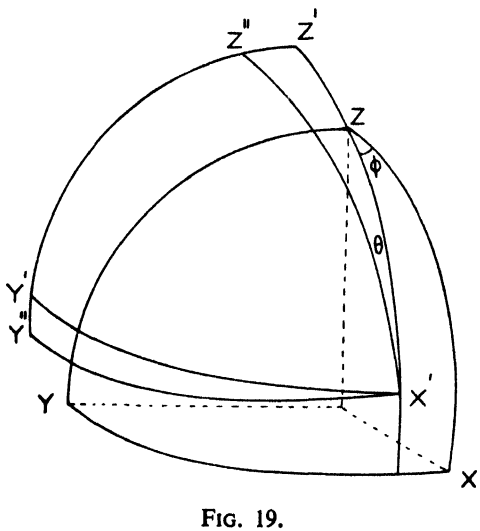


FIG. 19.

OZ′ is the direction in which the axis of the molecule is situated initially. The rotation axis may be chosen to be in the plane containing OZ and OZ′ axes to start with, without any loss of generality. In the initial position, the direction cosines may be written as

	X	Y	Z
X′	$\sin\theta \cos\varphi$	$\sin\theta \sin\varphi$	$\cos\theta$
Y′	$-\sin\varphi$	$\cos\varphi$	0
Z′	$-\cos\theta \cos\varphi$	$-\cos\theta \sin\varphi$	$\sin\theta$

Assuming that the incident light vector is one unit, p_z and p_y, the components of the moments induced in the molecule may be written as

$$p_z = C \sin^2\theta + A \cos^2\theta,$$

$$p_y = (A-C) \sin\theta \cos\theta \sin\varphi.$$

After a small interval of time t, if the molecule has a frequency of rotation ν, the direction cosines and the moments may be written as

	X	Y	Z
X′	$\sin\theta \cos\phi$	$\sin\theta \sin\phi$	$\cos\theta$
Y″	$\sin 2\pi\nu t \cos\phi \cos\theta$ $-\cos 2\pi\nu t \sin\phi$	$\sin 2\pi\nu t \sin\phi \cos\theta$ $+\cos 2\pi\nu t \cos\phi$	$-\sin 2\pi\nu t \sin\theta$
Z″	$-\cos 2\pi\nu t \cos\phi \cos\theta$ $-\sin 2\pi\nu t \sin\phi$	$-\cos 2\pi\nu t \sin\phi \cos\theta$ $+\sin 2\pi\nu t \cos\phi$	$\cos 2\pi\nu t \sin\theta$

$$p_z = C \cos^2 2\pi\nu t \sin^2\theta + A \cos^2\theta + A \sin^2 2\pi\nu t \sin^2\theta,$$

$$p_y = (A-C)[\cos^2 2\pi\nu t \sin\varphi \sin\theta \cos\theta - \sin 2\pi\nu t \cos 2\pi\nu t \sin\theta \cos\varphi].$$

Each one of these components may be split up into two parts, one being independent of time and the other varying with time. Denoting these by suffixes 1 and 2 respectively, we have

$$p_{z1} = \frac{C+2A}{3} + (C-A)\left\{\frac{1}{6} - \frac{\cos^2\theta}{2}\right\}; \; p_{z2} = \frac{C-A}{2}\left\{\sin^2\theta \cos 4\pi\nu t\right\};$$

$$p_{y1} = \frac{C-A}{2} \sin\theta \cos\theta \sin\varphi; \quad p_{y2} = \frac{C-A}{2}\left\{\sin\varphi \sin\theta \cos\theta \cos 4\pi\nu t - \sin\theta \cos\varphi \sin 4\pi\nu t\right\}.$$

If each of these expressions is multiplied by the periodicity $\sin 2\pi\nu_0 t$ in the incident light wave, it is easily seen that the oscillating moments p_{z1} and p_{y1} will give rise to Rayleigh scattering, the intensities in each case being proportional to $\overline{p_{z1}^2}$ and $\overline{p_{y1}^2}$. If the averaging is effected, as has been done in chapter III, for all values of θ and φ, we have

$$\overline{p_{z1}^2} = \alpha^2 + \frac{\gamma^2}{45}; \quad \overline{p_{y1}^2} = \frac{\gamma^2}{60}.$$

p_{z2} and p_{y2} may be written, after absorbing the periodicity of the incident light, as

$$p_{z2} = \frac{(C-A)\sin^2\theta}{4}\left\{\sin 2\pi(\nu_0+2\nu)t + \sin 2\pi(\nu_0-2\nu)t\right\},$$

$$p_{y2} = \frac{(C-A)\sin\varphi \sin\theta \cos\theta}{4}\left\{\sin 2\pi(\nu_0+2\nu)t + \sin 2\pi(\nu_0-2\nu)t\right\} + \frac{(C-A)\sin\theta \cos\varphi}{4}\left\{\cos 2\pi(\nu_0+2\nu)t - \cos 2\pi(\nu_0-2\nu)t\right\}.$$

These expressions give rise to Raman scattering of frequency $\nu_0+2\nu$ and $\nu_0-2\nu$ in both the Z and Y components and their intensities will be proportional to $\overline{p_{z2}^2}$ and $\overline{p_{y2}^2}$ in each component respectively. On performing the averages, as before, we obtain

$$\overline{p_{z2}^2} = \frac{\gamma^2}{30} \text{ for } \nu_0+2\nu \text{ and } \frac{\gamma^2}{30} \text{ for } \nu_0-2\nu;$$

$$\overline{p_{y2}^2} = \frac{\gamma^2}{40} \text{ for } \nu_0+2\nu \text{ and } \frac{\gamma^2}{40} \text{ for } \nu_0-2\nu.$$

These are the results that are to be expected if plane polarized incident light is used. In all these cases the fourth power factor is omitted as has already been mentioned. If unpolarized light is used, it is easily seen that all the Y components are to be

doubled and the Z components enhanced by an amount equal to the Y component. In the following, the results for unpolarized incident light are given in brackets. Some important remarks may now be made. The intensities given above represent the average expectation per molecule and the total intensity from n molecules is, as before, n times that obtained for a single molecule. As in the case of the vibrational lines, the intensities of the Stokes and anti-Stokes rotational Raman lines are also apparently equal. The observed results are not, however, in agreement with this conclusion and the discrepancy is obviously due to the fact that there are not as many molecules which are in a position to part with their rotational energy as there are which are in a position to receive the energy. The intensities will therefore be in the ratio of the relative populations of these two sets of molecules. The aggregate value of the parallel component is $\alpha^2+\frac{4}{45}\gamma^2\,(\alpha^2+\frac{7}{45}\gamma^2)$ of which $\alpha^2+\frac{\gamma^2}{45}\,(\alpha^2+\frac{7}{180}\gamma^2)$ appears as Rayleigh scattering and $\frac{3}{45}\gamma^2\,(\frac{21}{180}\gamma^2)$ appears as Raman scattering. The aggregate agrees with what has been obtained for non-rotating molecules in chapter III (see 24*a* and 25*a*). The aggregate value of the perpendicular component is $\frac{3}{45}\gamma^2\,(\frac{6}{45}\gamma^2)$ of which $\frac{\gamma^2}{60}\left(\frac{\gamma^2}{30}\right)$ appears as Rayleigh scattering and $\frac{\gamma^2}{20}\left(\frac{\gamma^2}{10}\right)$ appears as Raman scattering. The aggregate again agrees with that obtained for a non-rotating molecule. The shift in frequency of the rotational Raman line is twice the frequency of rotation. The depolarization factor of that part of the scattering which is strictly of the Rayleigh type is only

$$\frac{\gamma^2/60}{\alpha^2+\gamma^2/45}\left(\frac{\gamma^2/30}{\alpha^2+\frac{7}{180}\gamma^2}\right).$$

These expressions replace 24*a* and 25*a* of chapter III. The depolarization factor of the rotational Raman scattering is $\frac{3}{4}$ $(\frac{6}{7})$. The intensity of the rotational Raman scattering is determined solely by the optical anisotropy of the molecule.

Defects in the Simple Picture.—The considerations set forth in the foregoing sections furnish an elementary description of the

mechanism of Raman scattering but the treatment is defective and incomplete in several respects. It looks as if only such of those molecules which are already oscillating or rotating can give rise to Raman lines, since it has been assumed that the oscillation or the rotation of the molecule furnishes the requisite periodicity. With the help of the Boltzmann law, it may, however, be shown that molecules which are intrinsically in a state of oscillation are quite small in number at ordinary temperatures. This number decreases very rapidly with increasing vibration frequency and assumes negligible proportions at high frequencies. The majority of the molecules in a medium do not therefore apparently contribute to the production of Raman lines. Such a conclusion is not consistent with the appreciable intensity with which we are able to record vibrational Raman lines characterized by quite large shifts. Another consequence of the theory, which is obviously incorrect, is in respect of the relative intensities of the Stokes and anti-Stokes Raman lines, both of which apparently arise from the same molecule and therefore possess the same intensity. As a matter of fact, the Stokes lines are much stronger than the anti-Stokes lines and this difficulty could be got over only by introducing *ad hoc* considerations with regard to the relative populations. The theory is also defective since a quantization of the rotational energy is not contemplated at all and accordingly there is no means of calculating separately the intensities of the individual rotational Raman lines. A fuller and more rigorous treatment based on quantum theory removes all these difficulties and will be given in the following sections.

Kramers-Heisenberg Dispersion Formula.[1]—The induced moment p will now be regarded as a matrix. All the diagonal elements of this matrix will be responsible for Rayleigh scattering in the various stationary states of the molecule and the non-diagonal elements will give rise to Raman scattering. If a mole-

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[1] A very complete treatment has been given by Placzek in *Handbuch Der Radiologie*, *6*, part 2, 205 (1934). The treatment given here closely follows this but has been simplified in several respects and deals with only the more essential aspects.

cule finds itself in the field of a light wave[1] $\frac{U}{2}e^{2\pi i\nu_0 t}+\frac{U^*}{2}e^{-2\pi i\nu_0 t}$, the matrix elements of its electric moment M undergo alterations as per the scheme

$$\mathrm{M}_{kk}=\overset{0}{\mathrm{M}}_{kk}+\overset{(1)}{\mathrm{M}}_{kk};\quad \mathrm{M}_{kn}=\overset{0}{\mathrm{M}}_{kn}+\overset{(1)}{\mathrm{M}}_{kn};$$

where

$$\overset{(1)}{\mathrm{M}}_{kk}=p_{kk}\,e^{2\pi i\nu_0 t}+p^*_{kk}\,e^{-2\pi i\nu_0 t},$$

$$p_{kk}=\frac{1}{2h}\sum_r\left\{\frac{(U\mathrm{M}_{kr})\,\mathrm{M}_{rk}}{\nu_{rk}-\nu_0}+\frac{\mathrm{M}_{kr}\,(U\mathrm{M}_{rk})}{\nu_{rk}+\nu_0}\right\}.\quad ..\quad (1)$$

The unstarred letters are generally complex quantities. In such a case, the starred letters are also complex and are conjugate to the original ones. In case we are dealing with real quantities, the distinction disappears. The double suffix kk implies that the matrix element is associated with the stationary state k. M_{kk} and $\overset{0}{\mathrm{M}}_{kk}$ are respectively the values of this element in the presence and absence of the external field. Since $\overset{(1)}{\mathrm{M}}_{kk}$ is an oscillating moment, the molecule will emit light according to the usual laws of radiation. The frequency of the emitted radiation will be ν_0 and its intensity (see 4 of chapter III) will be given by (2).

$$\frac{64\pi^4\nu_0^4}{3c^3}\left|p_{kk}\right|^2.\quad ..\quad ..\quad ..\quad (2)$$

Similarly, $\overset{(1)}{\mathrm{M}}_{kn}$ which refers to the two stationary states k and n, may be written as

$$\overset{(1)}{\mathrm{M}}_{kn}=p_{kn}e^{2\pi i(\nu_{kn}+\nu_0)t}+p^*_{kn}e^{-2\pi i(\nu_{kn}+\nu_0)t}$$
$$+p'_{kn}e^{2\pi i(\nu_{kn}-\nu_0)t}+p'^*_{kn}e^{-2\pi i(\nu_{kn}-\nu_0)t},$$

where

$$p_{kn}=\frac{1}{2h}\sum_r\left\{\frac{(U\mathrm{M}_{kr})\mathrm{M}_{rn}}{\nu_{rk}-\nu_0}+\frac{\mathrm{M}_{kr}(U\mathrm{M}_{rn})}{\nu_{rn}+\nu_0}\right\}.\quad ..\quad (3)$$

and p'_{kn} is obtained from p_{kn} by replacing ν_0 in it by $-\nu_0$. $\overset{(1)}{\mathrm{M}}_{kn}$ is again an oscillating moment and the molecule will

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[1] In the special case where $U_x=U_y=0$ and $U_z=\mathrm{E}_0$, the incident light vector reduces to $\mathrm{E}_0\cos 2\pi\nu_0 t$ and represents a linearly polarized beam.

emit radiation. The frequency of the emitted radiation will no longer be ν_0 but will be either $\nu_{kn}+\nu_0$ or $\nu_{kn}-\nu_0$. Thus we get a general explanation of the appearance of altered frequencies in the spectrum of the scattered light. The dashed terms are called the negative dispersion terms and the condition that scattered light relating to these terms may appear is that $\nu_{kn}-\nu_0 > 0$ or $E_k > h\nu_0+E_n$. If the inducing agency is visible light of frequency ν_0, the molecule will be obliged to find itself in an electronically excited state in order that these transitions may occur. Such transitions have not yet been detected and these terms will not be considered hereafter. The undashed terms are the usual dispersion terms and the condition, that scattered light relating to these terms may appear, is that $\nu_{kn}+\nu_0 > 0$ or $E_n < h\nu_0+E_k$. Both kinds of transitions, namely those in which $E_n > E_k$ and those in which $E_n < E_k$, satisfy this condition and we accordingly get two types of Raman lines. If k is taken as the initial state, the former are called the Stokes Raman lines and the latter are called the anti-Stokes Raman lines. The frequency of the emitted radiation will be $\nu_{kn}+\nu_0$ and its intensity per molecule is given by (4).

$$\frac{64\pi^4(\nu_{kn}+\nu_0)^4}{3c^3}\left|p_{kn}\right|^2. \qquad \ldots \qquad \ldots \qquad (4)$$

In order that a line of altered frequency $\nu_0+\nu_{kn}$ may be emitted as a result of the system undergoing a transition from state k to state n, p_{kn} should not vanish. The summation in (3) extends over all the intermediate states r. Only such of these which are capable of combining in ordinary absorption with both the initial and final states k and n will contribute to the value of p_{kn}, as it is only then that the terms M_{kr} and M_{rn} do not vanish. The existence of a Raman line due to a transition $k \rightarrow n$ may therefore be said to depend upon the existence of some intermediate levels r such that the transitions $k \rightarrow r$ and $r \rightarrow n$ are allowed in ordinary absorption.[1]

Stokes and Anti-Stokes Raman Lines.—As has already been said, the radiations of altered frequencies emitted by different

[1] The derivation of (1) and (3) was first given by Kramers and Heisenberg in connection with the dispersion theory. See Z. f. Phys., *31*, 681 (1925).

molecules are incoherent, owing to the presence of arbitrarily varying phase factors. If there are N_k molecules in the kth state which is of a lower energy and N_n in the nth state which is of a higher energy, we can easily see from (4) that the average intensity of the line arising from a transition $k \rightarrow n$ is proportional to $N_k (\nu_0 - \nu_{nk})^4$ while that arising from the reverse transition $n \rightarrow k$ is proportional to $N_n (\nu_0 + \nu_{nk})^4$. The former is the Stokes line and the latter is the anti-Stokes line. Denoting their intensities by I_S and I_A respectively, we have

$$\frac{I_A}{I_S} = \frac{N_n (\nu_0 + \nu_{nk})^4}{N_k (\nu_0 - \nu_{nk})^4}. \quad \ldots \quad \ldots \quad \ldots \quad (5)$$

Combining this with the Boltzmann relation, $N_n/N_k = e^{-h\nu_{nk}/kT}$, we obtain [1]

$$\frac{I_A}{I_S} = \left(\frac{\nu_0 + \nu_{nk}}{\nu_0 - \nu_{nk}}\right)^4 e^{-h\nu_{nk}/kT}. \quad \ldots \quad \ldots \quad (6)$$

Relation between the Induced Moments and the Polarizability Tensor.—It is clear from (2) and (4) that an explicit evaluation of the intensity of Rayleigh and Raman scattering, in any particular case, rests upon our being able to evaluate the matrix elements p_{kk} and p_{kn}. Although, this may be done in specially simple cases, numerous difficulties present themselves when we tackle more complicated ones. This procedure is, however, not necessary and many of the laws governing the Raman scattering may be deduced in an indirect way, as has been shown by Placzek. A tensor relationship of the form given below [2] should exist between the incident vector U and the induced moment vector p_{kn}.

$$(p_x)_{kn} = \sum_y (\alpha_{xy})_{kn} U_y, \quad \ldots \quad \ldots \quad \ldots \quad (7)$$

where

$$(\alpha_{xy})_{kn} = \frac{1}{h} \sum_r \left\{ \frac{(M_y)_{kr} (M_x)_{rn}}{\nu_{rk} - \nu_0} + \frac{(M_x)_{kr} (M_y)_{rn}}{\nu_{rn} + \nu_0} \right\}. \quad \ldots \quad (8)$$

---

[1] In deriving this, we have assumed that $|p_{kn}|^2$ and $|p_{nk}|^2$ are identical. This is true since p, which is a real quantity, is represented by a *Hermitean matrix.*

[2] Hereafter, the amplitude of the incident field, the polarizability tensor and the induced moment will be regarded as real quantities only.

In view of the relationship (8), we can derive the general laws by considering the behaviour of α, which is an experimentally determinable quantity, and thus avoid the necessity of having to explicitly perform the summations in (1) and (3). The intensity of scattering depends on p's and therefore on the components of α. We have, accordingly, to study the behaviour of the tensor components α_{xy} relating to each one of the matrix elements.

The following relationships are easily understood.

$$\alpha_{xy} = \alpha_0 \delta^x_y + \alpha^s_{xy}, \quad \ldots \quad \ldots \quad \ldots \quad (9)$$

where $\delta^x_y = 1$ or 0 according as $x = y$ or $x \neq y$.

$$\alpha_0 = \tfrac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) = \tfrac{1}{3}(A+B+C), \quad \ldots \quad (10)$$

$$\alpha_{xy} = \sum_{x'y'} \alpha'_{xy} \cos xx' \cos yy'. \quad \ldots \quad \ldots \quad (11)$$

The first term in (9) is the isotropic portion of the tensor and is an invariant under a rotation of the co-ordinate axes. The second term which is the anisotropic portion is a symmetric tensor with the sum of the diagonal terms always equal to zero. The tensor components α_{xy}, relating to the system of axes fixed in space, are given in terms of α'_{xy}, relating to the system of axes fixed in the molecule, by equations of the type (11). The intensity of a Raman line depends on $(\alpha_{xy})^2$, i.e. on $(\alpha_0 \delta^x_y + \alpha^s_{xy})^2$. In obtaining the average intensity for a case where the molecules are randomly oriented in space, all cross products vanish and $(\alpha_0 \delta^x_y + \alpha^s_{xy})^2$ may, in effect, be written as

$$\delta^x_y (\alpha_0)^2 + (\alpha^s_{xy})^2. \quad \ldots \quad \ldots \quad \ldots \quad (12)$$

The intensities of the isotropic and the anisotropic scattering are therefore additive.

Intensity and Polarization Characters.—Let us consider the special case of plane polarized incident light given by

$$E_x = 0; \quad E_y = 0; \quad E_z = E = E_0 \cos 2\pi\nu_0 t. \quad \ldots \quad (13)$$

(13) corresponds to $U_x = U_y = 0$ and $U_z = E_0$ as has already been explained. We have

$$p_z = \alpha_{zz} E \quad \text{and} \quad p_y = \alpha_{yz} E. \quad \ldots \quad \ldots \quad (14)$$

In case we are dealing with Rayleigh scattering in the stationary state k, we have

$$I^z_{kk} \propto \overline{(\alpha_{zz})^2_{kk}} \quad \text{and} \quad I^y_{kk} \propto \overline{(\alpha'_{yz})^2_{kk}}.$$

The former may be written as the sum of two terms $(\alpha_0)^2_{kk}$ and $\overline{(\alpha'_{zz})^2_{kk}}$ and these may easily be evaluated in the manner already described for the case of random distribution [1]. I^y_{kk} is also evaluated in the same manner and dropping the suffixes and omitting the constants of proportionality, we obtain

$$I^z = \alpha_0^2 + \tfrac{4}{45}\gamma_0^2 ; \quad I^y = \tfrac{3}{45}\gamma_0^2 ;$$

$$\varrho_v = \frac{\tfrac{3}{45}\gamma_0^2}{\alpha_0^2 + \tfrac{4}{45}\gamma_0^2}. \qquad \qquad (15)$$

If A, B and C are the principal polarizabilities, the limiting case of an anisotropic molecule will be one in which A is finite and $B = C = 0$ giving $\alpha_0 = \frac{A}{3}$ and $\gamma_0^2 = A^2$. The upper limit for ϱ_v is therefore $\frac{1}{3}$ and the lower limit is zero. The corresponding expression, when incident unpolarized light is used, may easily be written out and the upper limit in that case obtained as $\frac{1}{2}$ instead of $\frac{1}{3}$.

In the case of Raman scattering, associated with a transition $k \rightarrow n$, we have

$$I^z_{kn} = (\alpha_0)^2_{kn} + \tfrac{4}{45}(\gamma_0)^2_{kn} ; \quad I^y_{kn} = \tfrac{3}{45}(\gamma_0)^2_{kn} ;$$

$$\varrho_v = \frac{\tfrac{3}{45}(\gamma_0)^2_{kn}}{(\alpha_0)^2_{kn} + \tfrac{4}{45}(\gamma_0)^2_{kn}}. \qquad \qquad (16)$$

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[1] For simplicity, we are here considering the case of random distribution. In the rigorous treatment of the subject, we should consider the rotational quantum number J of the molecule in question and the permitted orientations will be only $2J+1$. The molecule may pass over from any one of these to any other permitted orientation in the excited state, the transitions being subject to the usual selection rules. The summations should be over these discrete states and not for all orientations. It will, however, be seen later that in most cases the two methods lead to identical results when we are dealing with aggregate intensities.

It may be seen from (16), that the upper limit for ϱ_v is $\frac{3}{4}$ and occurs when $(\alpha_0)_{kn}$ is zero. This is always satisfied for the anisotropic portion of the tensor since it is characterized by the fact that the sum of the diagonal terms is zero. Accordingly, vibrational Raman lines in which there is no isotropic radiation are depolarized to the limit. Another instance of this type is the case of a rotational Raman line. It has already been remarked that α_0, which is the sum of the diagonal terms of the tensor, is an invariant under a rotation of the axes and therefore $(\alpha_0)_{kn}$, where k and n represent two different rotational states of a molecule, is zero. Accordingly the rotational Raman lines are always depolarized to the limit. The expression corresponding to (16), when incident unpolarized light is used, may easily be written out and the upper limit in that case obtained as $\frac{6}{7}$.

We shall now consider the case of incident circularly polarized light[1] given by $E_x = E_0 \cos 2\pi\nu_0 t$; $E_y = E_0 \sin 2\pi\nu_0 t$; $E_z = 0$; $E_x + iE_y = E_0 e^{2\pi i\nu_0 t}$. In the place of (14), we have

$$(p_x + ip_y)_{kn} = (\alpha_{xx} + i\alpha_{yx})_{kn} E_x + (\alpha_{xy} + i\alpha_{yy}) E_y$$

$$= E_0 \left\{ \left(\frac{\alpha_{xx} + \alpha_{yy}}{2} \right)_{kn} e^{2\pi i\nu_0 t} + \left(\frac{\alpha_{xx} - \alpha_{yy} + 2i\alpha_{xy}}{2} \right)_{kn} e^{-2\pi i\nu_0 t} \right\}.$$

The first and the second terms correspond respectively to emitted light that is circularly polarized in the same sense as the incident light and to that which is circularly polarized in a reverse sense. Their intensities will be respectively proportional to

$$\overline{\left(\frac{\alpha_{xx} + \alpha_{yy}}{2} \right)_{kn}^2} \text{ and } \overline{\left(\frac{\alpha_{xx} - \alpha_{yy} + 2i\alpha_{xy}}{2} \right)_{kn}^2}.$$

Denoting these by I_c and I_r respectively, we have

$$I_c = (\alpha_0)_{kn}^2 + \tfrac{1}{45}(\gamma_0)_{kn}^2 ; \quad I_r = \tfrac{2}{15}(\gamma_0)_{kn}^2.$$

The reversal factor P is given by (17).

$$P = \frac{\tfrac{2}{15}(\gamma_0)_{kn}^2}{(\alpha_0)_{kn}^2 + \tfrac{1}{45}(\gamma_0)_{kn}^2}. \quad \ldots \quad \ldots \quad (17)$$

[1] This corresponds to $U_x = iU_y = E_0$; $E_z = 0$.

Combining this with (15), we obtain

$$\mathrm{P} = \frac{2\varrho_v}{1-\varrho_v} \text{ or alternatively } \mathrm{P} = \frac{\varrho}{1-\varrho}.$$

The limits for P are obviously 0 and 6 since the limits for ϱ_v are 0 and $\frac{3}{4}$ and for ϱ are 0 and $\frac{6}{7}$.

Vibrational Raman Scattering.—It has been shown in the foregoing sections that the intensity of a Raman line $k \rightarrow n$ depends on the existence of p_{kn} and therefore on the existence of α_{kn}. If we regard the molecule as changing from a particular vibrational state v to another vibrational state v', there being no change in the electronic energy, we may write α_{kn} as $\alpha_{vv'}$. This matrix element will no doubt have a unique value for a given position of the nuclei but will not be unique, if we are dealing with any given quantum state since the nuclei may occupy a range of positions permitted in that state. When we are interested in evaluating the scattering moment pertaining to a definite quantum state, we have accordingly to obtain the average value of α over the entire range of permitted configurations of the nuclei. If α has the value $\alpha(q)$ for a particular position q of the nuclei, we have

$$\alpha_{vv'} = \int \psi^*_{v'}(q)\, \alpha(q)\, \psi_v(q)\, dq. \qquad \ldots \qquad \ldots \qquad (18)$$

We may expand $\alpha(q)$ in the form

$$\alpha(q) = \alpha_0 + \sum_j \left(\frac{\partial \alpha}{\partial q_j}\right)_0 q_j + \tfrac{1}{2} \sum_{jk} \left(\frac{\partial^2 \alpha}{\partial q_j \partial q_k}\right)_0 q_j q_k + \tfrac{1}{6} \sum_{jkl} \left(\frac{\partial^3 \alpha}{\partial q_j \partial q_k \partial q_l}\right)_0 q_j q_k q_l, \text{ etc.} \qquad \ldots \qquad (19)$$

q_j, q_k, etc., are the various normal co-ordinates of the molecule and a particular set of values of q_j, q_k, etc., define a configuration q of the molecule. The set $q_j=0$, $q_k=0$, etc., correspond to the equilibrium configuration. A set of vibrational quantum numbers v_j, v_k, etc., define a state v. Substituting (19) in (18) and integrating, we have[1]

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[1] The method of evaluating these integrals is indicated in Appendix IV.

$$\alpha_{vv} = \alpha_0 + \tfrac{1}{2}\sum_j \left(\frac{\partial^2\alpha}{\partial q_j^2}\right)_0 (q_j^2)_{vv} = \alpha_0 + \tfrac{1}{2}\sum_j \left(\frac{\partial^2\alpha}{\partial q_j^2}\right)_0 (2v_j+1)C_j\,,$$

$$\alpha_{v_j,v_j+1} = \left(\frac{\partial\alpha}{\partial q_j}\right)_0 (q_j)_{v_j,v_j+1} + \tfrac{1}{6}\left(\frac{\partial^3\alpha}{\partial q_j^3}\right)_0 (q_j^3)_{v_j,v_j+1}$$

$$+ \tfrac{1}{6}\sum_k \left(\frac{\partial^3\alpha}{\partial q_j \partial q_k^2}\right)_0 (q_j)_{v_j,v_j+1}(q_k^2)_{v_k,v_k}\cdots\cdots$$

$$= C_j^{\frac{1}{2}}\sqrt{v_j+1}\left\{\left(\frac{\partial\alpha}{\partial q_j}\right)_0 + \tfrac{1}{2}\left(\frac{\partial^3\alpha}{\partial q_j^3}\right)_0 C_j(v_j+1)\right.$$

$$\left. + \tfrac{1}{6}\sum_k \left(\frac{\partial^3\alpha}{\partial q_j \partial q_k^2}\right)_0 C_k(2v_k+1)\right\},$$

$$\alpha_{v_j,\,v_j+2} = \tfrac{1}{2}\left(\frac{\partial^2\alpha}{\partial q_j^2}\right)_0 (q_j^2)_{v_j,\,v_j+2}\cdots = \tfrac{1}{2}\left(\frac{\partial^2\alpha}{\partial q_j^2}\right)_0 C_j\sqrt{(v_j+1)(v_j+2)}\,,$$

$$\alpha_{v_j,\,v_j+3} = \tfrac{1}{6}\left(\frac{\partial^3\alpha}{\partial q_j^3}\right)_0 (q_j^3)_{v_j,\,v_j+3}\cdots = \tfrac{1}{6}\left(\frac{\partial^3\alpha}{\partial q_j^3}\right)_0 C_j^{\frac{3}{2}}\sqrt{(v_j+1)(v_j+2)(v_j+3)},$$

$$\alpha_{v_j,\,v_j+1\,;\,v_k,\,v_k+1} = \tfrac{1}{2}\left(\frac{\partial^2\alpha}{\partial q_j \partial q_k}\right)_0 (q_j)_{v_j,\,v_j+1}(q_k)_{v_k,\,v_k+1}\cdots\cdots$$

$$= \tfrac{1}{2}\left(\frac{\partial^2\alpha}{\partial q_j\,\partial q_k}\right)_0 \sqrt{C_jC_k(v_j+1)(v_k+1)}\,. \qquad \cdots (20)$$

In the above relations $C_j = \dfrac{h}{8\pi^2\nu_j\mu_j}$, where μ_j is the reduced mass and ν_j is the corresponding vibration frequency.

In the simple case of a diatomic molecule with one vibrational degree of freedom, omitting the higher order terms, we may easily see that if the intensity of the Rayleigh line is given by $\alpha_0^2 + \frac{4}{45}\gamma_0^2$, that of the Raman line $0 \rightarrow 1$ is given by

$$C_j\left\{\left(\frac{d\alpha}{dr}\right)_0^2 + \tfrac{4}{45}\left(\frac{d\gamma}{dr}\right)_0^2\right\}.$$

This is based on a formal extension of the above treatment which shows that just as α_0^2 is replaced by $C_j\left(\frac{d\alpha}{dr}\right)_0^2$, γ_0^2 is also replaced by $C_j\left(\frac{d\gamma}{dr}\right)_0^2$. In this case, the only normal co-ordinate r represents the variation in the distance between the nuclei and dr takes the place of dq. This expression gives the parallel component when plane polarized incident light is used. The perpendicular component will similarly be $C_j \cdot \frac{3}{45}\left(\frac{d\gamma}{dr}\right)_0^2$. After substituting the value of C_j and multiplying the numerator and denominator by r_0, the equilibrium nuclear distance, the intensities given in (21) are obtained.

$$I^z_{0\to1} = \frac{h}{8\pi^2\nu I}(\alpha'^2 + \tfrac{4}{45}\gamma'^2),$$

$$I^y_{0\to1} = \frac{h}{8\pi^2\nu I} \cdot \tfrac{3}{45}\gamma'^2. \qquad (21)$$

I is the moment of inertia and α' and γ' have the same significance as has been assigned to them earlier in this chapter. These expressions are identical with those already derived from elementary considerations. Appropriate additions to I^z and I^y may easily be effected for the case of unpolarized incident light. All the laws that have already been deduced in respect of the polarization characters easily follow. If the series in (19) is assumed to be rapidly convergent, it follows that the overtones in Raman effect will generally be very faint even when they are permitted by the selection rules to appear.

It is further obvious that for a Raman line to occur with appreciable intensity, either $\left(\frac{\partial\alpha}{\partial q}\right)_0$ or $\left(\frac{\partial\gamma}{\partial q}\right)_0$ or both should not vanish. Intense Raman lines corresponding to particular oscillations will accordingly result, if the mean polarizability or the anisotropy of the molecule varies considerably with a variation of the concerned normal co-ordinate. If the variations are comparatively small, the lines are weak. If only $\left(\frac{\partial\alpha}{\partial q}\right)_0$ exists, the resulting Raman line is perfectly polarized and if

only $\left(\frac{\partial\gamma}{\partial q}\right)_0$ exists, the resulting Raman line is depolarized to the limit. In intermediate cases, we obtain intermediate values. The selection rules and the conditions under which these extremes occur will be considered in greater detail in the next chapter.

Rotational Raman Scattering.—No attempt has hitherto been made to calculate the intensity of the individual rotational lines or of the total rotational scattering as apart from the vibrational or Rayleigh scattering. The expressions so far given relate to the aggregate effect arising from the molecules in each one of the rotational states in the vibrational state v passing over into all the rotational states of v' permitted by the appropriate selection rules. In case where $v = v'$, part of the total intensity will be arising from pure rotational Raman scattering and in case $v \neq v'$, a part will similarly be due to rotational Raman scattering in which there is a change in the vibrational energy as well. The selection rules for rotational Raman scattering have also not been derived explicitly. These problems will be considered in this section.

In the place of the cartesian co-ordinates x, y, z, we now introduce circular co-ordinates $\frac{1}{\sqrt{2}}(x+iy)$, $\frac{1}{\sqrt{2}}(x-iy)$ and z and denote them by the suffixes 1, -1 and 0. r, θ and φ represent the polar co-ordinates. We have the following relationships between the co-ordinates, direction cosines, vector components and the tensor components in the different systems of co-ordinates (see Appendix V).

$$\frac{1}{\sqrt{2}}(x+iy) = \frac{1}{\sqrt{2}} r \sin\theta\, e^{i\phi}\,; \quad \frac{1}{\sqrt{2}}(x-iy) = \frac{1}{\sqrt{2}} r \sin\theta\, e^{-i\phi}\,;$$

$$z = r\cos\theta\,.$$

$$D_{0\,0} = D_{zz'}$$

$$D_{0\,1} = D^{*}_{0\,-1} = \frac{1}{\sqrt{2}}(D_{zx'} + iD_{zy'})$$

$$D_{1\,0} = D^{*}_{-1\,0} = \frac{1}{\sqrt{2}}(D_{xz'} + iD_{yz'})$$

$$D_{1\,-1} = D^{*}_{-1\,1} = \tfrac{1}{2}\,[(D_{xx'} + D_{yy'}) + i(D_{yx'} - D_{xy'})]$$

$$\mathrm{D}_{11} = \mathrm{D}^{*}_{-1\,-1} = \tfrac{1}{2}\,[(\mathrm{D}_{xx'} - \mathrm{D}_{yy'}) + i(\mathrm{D}_{yx'} + \mathrm{D}_{xy'})]\,.$$

$$\mathrm{M}_1 = \frac{1}{\sqrt{2}}(\mathrm{M}_x + i\mathrm{M}_y)\,; \quad \mathrm{M}_{-1} = \frac{1}{\sqrt{2}}(\mathrm{M}_x - i\mathrm{M}_y)\,; \quad \mathrm{M}_0 = \mathrm{M}_z\,.$$

$$\alpha_{1\,1} = \alpha^{*}_{-1\,-1} = \tfrac{1}{2}\,(\alpha_{xx} - \alpha_{yy}) + \frac{i}{2}(\alpha_{xy} + \alpha_{yx})$$

$$\alpha_{-1\,1} = \alpha_{1\,-1} = \tfrac{1}{2}\,(\alpha_{xx} + \alpha_{yy})$$

$$\alpha_{1\,0} = \alpha_{0\,1} = \frac{1}{\sqrt{2}}(\alpha_{xz} + i\alpha_{yz})$$

$$\alpha_{-1\,0} = \alpha_{0\,-1} = \frac{1}{\sqrt{2}}(\alpha_{xz} - i\alpha_{yz})$$

$$\alpha_{0\,0} = \alpha_{zz}.$$

In the above equations D stands for the cosine of the angle between the co-ordinate axes indicated by the suffixes. The extended meaning of such a direction cosine in the case of circular co-ordinates will be clear from Appendix V. In the place of (7), (9), (10) and (11) we have (7*a*), (9*a*), (10*a*) and (11*a*) respectively. The suffixes λ and μ denote that the components relate to the circular co-ordinates.

$$p_\lambda = \sum_{\mu} \alpha_{\lambda\mu}\, U_{-\mu}\,, \qquad \ldots \qquad (7a)$$

$$\alpha_{\lambda\mu} = \alpha_0 \delta^{\lambda}_{-\mu} + \alpha^{s}_{\lambda\mu}\,, \qquad \ldots \qquad (9a)$$

$$\alpha_0 = \tfrac{1}{3}\,(\alpha_{0\,0} + \alpha_{1\,-1} + \alpha_{-1\,1})\,, \qquad \ldots \qquad (10a)$$

$$\alpha_{\lambda\mu} = \sum_{\lambda'\mu'} \alpha'_{\lambda\mu}\, \mathrm{D}_{\lambda-\lambda'}\, \mathrm{D}_{\mu-\mu'}\,. \qquad \ldots \qquad (11a)$$

The transformation of a vector from one set of axes to another is according to the equation $p_\lambda = \sum_{\lambda'} p'_\lambda\, \mathrm{D}_{\lambda-\lambda'}$ in the place of $p_x = \sum_{x'} p_x' \cos x\, x'$. The selection rules may now be easily obtained. The intensity of direct absorption depends on quantities like M_{kn} which are the matrix elements of the electric moment. These elements may be evaluated with the help of (22). The intensity of the Raman line due to a transition $k \rightarrow n$ depends upon quantities like α_{kn}. These may be evaluated with the help of (23).

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$$\left(M_\lambda\right)_{kn} = \int M_\lambda \psi_n^* \psi_k d\tau \cdot \quad \ldots \quad \ldots \quad (22)$$

$$\left(\alpha_{\lambda\mu}\right)_{kn} = \int \alpha_{\lambda\mu} \psi_n^* \psi_k d\tau \cdot \quad \ldots \quad \ldots \quad (23)$$

The conditions under which the above integrals do not vanish, have now to be investigated. In polar co-ordinates, the wave functions may be split into three parts, each depending respectively on r, θ and φ. We need consider only that part of the wave function which depends on φ and the relevant factor for ψ_m is $e^{im\phi}$. Accordingly, the dependence of $\psi_{s'm'}^*$ ψ_{sm} on φ will be determined by the factor $e^{i(m-m')\phi}$. $s'm'$ and sm stand for the quantum numbers n and k respectively. m denotes the projection of the angular momentum on the Z axis and s denotes all the rest of the quantum numbers. We also see that M_λ contains the factor $e^{i\lambda\phi}$, where λ is successively 1, -1 and 0. We accordingly obtain for absorption

$$(M_\lambda)_{sm\,.\,s'm'} \propto \int e^{i\lambda\phi}\, e^{i(m-m')\phi}\, d\varphi\,,$$

where λ is successively equal to 1, -1 and 0. These integrals do not vanish only when

$$m'-m = \pm 1 \text{ or } 0.$$

The former pair corresponds to circularly polarized components whereas the latter is a plane polarized parallel component. Similarly the dependence of the tensor component $\alpha_{\lambda\mu}$ on φ will be determined by the factor $e^{i(\lambda+\mu)\phi}$. In the case of Raman scattering, we therefore have

$$(\alpha_{\lambda\mu})_{sm\,.\,s'm'} \propto \int e^{i(\lambda+\mu)\phi}\, e^{i(m-m')\phi}\, d\varphi\,.$$

$\lambda+\mu$ may have any of the values 0, ± 1, ± 2 since λ and μ may each be either 1, -1 or 0. The integral does not vanish only when

$$m'-m = \lambda+\mu = 0,\ \pm 1,\ \pm 2.$$

The tensor components that are responsible for the isotropic scattering are the diagonal ones, $\alpha_{0\,0}$, $\alpha_{1\,-1}$ and $\alpha_{-1\,1}$ (see 10a), and hence $m'-m = 0$ is the selection rule for this type of scattering. Anisotropic scattering arises from all the transitions $m'-m = 0$, ± 1, ± 2. It will be seen later that the corres-

ponding selection rules for J are respectively $\triangle J = 0$ and $\triangle J = 0, \pm 1, \pm 2$. These selection rules hold good generally but in special cases where the molecule possesses particular types of symmetry, there may be further restrictions imposed. For example, in a linear molecule, the entire angular momentum is confined to the plane of symmetry and the transitions $\triangle J = \pm 1$ disappear. $\triangle J = 0, \pm 2$ are the only allowed transitions.[1]

If $(\alpha_{xy})^{sm}_{s'm'}$ denotes a typical matrix element involving a transition $m \rightarrow m'$ in the rotational state, the intensity of the corresponding Raman line will obviously be determined by the squares of such elements. The intensity of a particular rotational line $J \rightarrow J'$ will be determined by terms like

$$\sum_m \sum_{m'} \left| (\alpha_{xy})^{sm}_{s'm'} \right|^2 .$$

The summation extends over all possible values of m and m'. This arises out of the fact that a molecule with an angular momentum quantum number J can have $2J+1$ different possible values of m and each one of these is equally probable. The appropriate factor, that enters the intensity calculations in respect of each of the molecules possessing the quantum number J in the initial state, will therefore be

$$\frac{1}{2J+1} \sum_m \sum_{m'} \left| (\alpha_{xy})^{sm}_{s'm'} \right|^2 .$$

The corresponding expression in the circular co-ordinates will be

$$\frac{1}{2J+1} \sum_m \sum_{m'} \left| (\alpha_{\lambda\mu})^{sm}_{s'm'} \right|^2 .$$

We shall now make use of the relation

$$(\alpha_{\lambda\mu})^{sm}_{s'm'} = \int \alpha_{\lambda\mu} \psi^*_{s'm'} \psi_{sm} d\tau . \quad .. \quad .. \quad (24)$$

Combining this with (11*a*), we have

$$(\alpha_{\lambda\mu})^{sm}_{s'm'} = \delta^{m'-m}_{\lambda'+\mu'} \int \sum_{\lambda'\mu'} (\alpha'_{\lambda\mu}) D_{\lambda-\lambda'} D_{\mu-\mu'} \psi^*_{s'm'} \psi_{sm} d\tau . \quad (25)$$

[1] This conclusion is valid only in the case of molecules whose ground state is a Σ state.

If, for simplicity, we assume that we are dealing with the case of diatomic molecules only and consider transitions in which there is no change in the vibrational quantum number, s and s' may be replaced by J and J$'$ and only those parts of the wave functions which involve m and J, i.e. φ and θ need be considered. The part of ψ which involves φ is merely $\frac{1}{\sqrt{2\pi}} e^{im\phi}$, and its effect has already been taken account of and is contained in the selection rule $m'-m = \lambda'+\mu' = \lambda+\mu$ and the symbol $\delta^{m'-m}_{\lambda'+\mu'}$ contains this fact. (25) will now be written as (25a).

$$(\alpha_{\lambda\mu})^{Jm}_{J'm'} = \delta^{m'-m}_{\lambda'+\mu'} \int \sum_{\lambda'\mu'} (\alpha'_{\lambda\mu})\, D_{\lambda-\lambda'}\, D_{\mu-\mu'}\, \Theta^{*}_{J'm'} \Theta_{Jm} \sin\theta\, d\theta\,. \quad \ldots \quad (25a)$$

$\Theta_{J'm'}$ and Θ_{Jm} are the normalized associated Legendre functions and since $d\tau$ is equal to $r^2 \sin\theta\, d\theta dr d\varphi$ in polar co-ordinates, the factor involving θ only is retained in (25a). The method of evaluating these integrals in the simple case of a diatomic molecule is indicated in Appendix IV. By squaring (25a) and summing up the result over all possible values of m for a given J, namely 0, ± 1 ..... $\pm$J, we obtain the following relations.

$$\sum_m \left| (\alpha_{0\,0})^{Jm}_{J'm} \right|^2 = \frac{1}{3}\left[G^0\right] + \frac{2}{15}\left[G^s\right]^J_{J'},$$

$$\sum_m \left| (\alpha_{1\,-1})^{Jm}_{J'm} \right|^2 = \frac{1}{3}\left[G^0\right] + \frac{1}{30}\left[G^s\right]^J_{J'},$$

$$\sum_m \left| (\alpha_{0\,1})^{Jm}_{J'm+1} \right|^2 = \sum_m \left| (\alpha_{0\,-1})^{Jm}_{J'm-1} \right|^2 = \frac{1}{10}\left[G^s\right]^J_{J'},$$

$$\sum_m \left| (\alpha_{1\,1})^{Jm}_{J'm+2} \right|^2 = \sum_m \left| (\alpha_{-1\,-1})^{Jm}_{J'm-2} \right| = \frac{1}{5}\left[G^s\right]^J_{J'},$$

where

$$[G^0] = 3(2J+1)\,|(\alpha_0)|^2,$$

$$\left[G^s\right]^J_{J'} = (2J+1)\cdot \tfrac{2}{3} b^J_{J'} \left|(\gamma_0)\right|^2. \quad \ldots \quad \ldots \quad (26)$$

α_0 is the mean polarizability given by (10a). γ_0 stands for the anisotropy of the tensor and is equal to $\alpha_0{}'_0 - \alpha_1{}'_{-1} = \alpha_0{}'_0 - \alpha_{-1}{}'_1$. The explicit values of $b^J_{J'}$ are given below.

$$b^{J}_{J} = \frac{J(J+1)}{(2J-1)(2J+3)},$$

$$b^{J}_{J\pm 1} = 0,$$

$$b^{J}_{J+2} = \frac{3}{2}\frac{(J+1)(J+2)}{(2J+1)(2J+3)},$$

$$b^{J}_{J-2} = \frac{3}{2}\frac{J(J-1)}{(2J+1)(2J-1)}. \quad \cdots \quad \cdots \quad (26a)$$

These values imply that the selection rule for J in such molecules is $\triangle J=0, \pm 2$. The depolarization factor for the anisotropic scattering, when linearly polarized incident light is used, easily follows as

$$\sum_{m}\left|\left(\alpha^{s}_{01}\right)^{Jm}_{J'm+1}\right|^{2} \Big/ \sum_{m}\left|\left(\alpha^{s}_{00}\right)^{Jm}_{J'm}\right|^{2} = \frac{3}{4}.$$

The reversal factor P is given by

$$\sum_{m}\left|\left(\alpha^{s}_{11}\right)^{Jm}_{J'm+2}\right|^{2} \Big/ \sum_{m}\left|\left(\alpha^{s}_{1\,-1}\right)^{Jm}_{J'm}\right|^{2} = 6.$$

Other results that have already been deduced may also be easily derived with the help of (26).

Intensities of the Individual Rotation Lines for a Symmetric Top Molecule.—This case differs from that of a diatomic molecule in possessing two different moments of inertia. A new quantum number K has to be introduced and the energy states of such a molecule are given by

$$W_{JK} = B\left[J(J+1)+\beta K^{2}\right]; \; B = \frac{h^{2}}{8\pi^{2}I_{A}}; \; \beta = \left(\frac{I_{A}}{I_{C}}-1\right). \quad (27)$$

K is the projection of J on the symmetry axis and has 2J+1 different values. I_C and I_A are the moments of inertia about the symmetry axis and an axis perpendicular thereto respectively. Placzek and Teller have evaluated the coefficients $[G^{a}]^{JK}_{J'K'}$ for the general case. Both the symmetric top and the diatomic molecule may be regarded as special cases and the appropriate expressions easily derived from the results of Placzek and Teller. The results of these authors will be quoted here.

Writing $[G^{a}]^{JK}_{J'K'} = (2J+1)\cdot\frac{2}{3}\cdot b^{JK}_{J'K'}\left|(\gamma_0)\right|^{2} \quad \cdots \quad \cdots \quad (28)$

TABLE XXXI

The Intensity Factors $b^{JK}_{J'K'}$ for the Rotational Raman Lines (According to Placzek and Teller).

K' \ J'	J	$J+1$	$J+2$
K ..	$\frac{[J(J+1)-3K^2]^2}{J(J+1)(2J-1)(2J+3)}$	$\frac{3K^2[(J+1)^2-K^2]}{J(J+1)(J+2)(2J+1)}$	$\frac{3[(J+1)^2-K^2][(J+2)^2-K^2]}{2(J+1)(J+2)(2J+1)(2J+3)}$
$K+1$ ..	$\frac{3(2K+1)^2(J-K)(J+K+1)}{2J(J+1)(2J-1)(2J+3)}$	$\frac{(J-2K)^2(J+K+1)(J+K+2)}{2J(J+1)(J+2)(2J+1)}$	$\frac{[(J+1)^2-K^2](J+K+2)(J+K+3)}{(J+1)(J+2)(2J+1)(2J+3)}$
$K-1$ ..	$\frac{3(2K-1)^2(J+K)(J-K+2)}{2J(J+1)(2J-1)(2J+3)}$	$\frac{(J+2K)^2(J-K+1)(J-K+2)}{2J(J+1)(J+2)(2J+1)}$	$\frac{[(J+1)^2-K^2](J-K+2)(J-K+3)}{(J+1)(J+2)(2J+1)(2J+3)}$
$K+2$ ..	$\frac{3[J^2-(K+1)^2][(J+1)^2-(K+1)^2]}{2J(J+1)(2J-1)(2J+3)}$	$\frac{[(J+1)^2-(K+1)^2](J+K+1)(J+K+3)}{2J(J+1)(J+2)(2J+1)}$	$\frac{(J+K+1)(J+K+2)(J+K+3)(J+K+4)}{4(J+1)(J+2)(2J+1)(2J+3)}$
$K-2$ ..	$\frac{3[J^2-(K-1)^2][(J+1)^2-(K-1)^2]}{2J(J+1)(2J-1)(2J+3)}$	$\frac{[(J+1)^2-(K-1)^2](J-K+1)(J-K+3)}{2J(J+1)(J+2)(2J+1)}$	$\frac{(J-K+1)(J-K+2)(J-K+3)(J-K+4)}{4(J+1)(J+2)(2J+1)(2J+3)}$

instead of (26), we can get the intensities of the individual rotation lines if $b^{JK}_{J'K'}$ is known. $b^{JK}_{J'K'}$ for various transitions $JK \rightarrow J'K'$ is given in Table XXXI. In order to get the factors relating to anti-Stokes lines, the following additional relationship should be used.

$$(2J+1)\, b^{JK}_{J'K'} = (2J'+1)\, b^{J'K'}_{JK} .$$

For a symmetric top molecule, the polarizability ellipsoid may also be taken as a spheroid and the selection rule for K comes out as $\triangle K = 0$. We accordingly get five branches of lines as per the scheme, given below, obtained by putting $\triangle K = 0$ in (27).

$$\nu_{J,\,J+2} = -(4J+6)\frac{B}{h} \ldots \text{S series};$$

$$\nu_{J+2,\,J} = (4J+6)\frac{B}{h} \ldots \text{O series};$$

$$\nu_{J,\,J+1} = -2\,(J+1)\frac{B}{h} \ldots \text{R series};$$

$$\nu_{J+1,\,J} = 2(J+1)\,\frac{B}{h} \ldots \text{P series};$$

$$\nu_{J,J} = 0 \ldots \text{Q series}.$$

In the case of a linear rotator, K itself is zero and the P and R branches do not appear at all, as may be expected. This is seen by putting $K = 0$ in the explicit values of $b^{JK}_{J'K}$ obtained from Table XXXI. These values are identical with those given under (26*a*) as may be expected.

For simplicity, it has been assumed in the foregoing derivations that there is no change in the vibrational quantum number. The results are, however, unaffected even if we consider a transition in which the vibrational quantum number v changes to v', as this does not affect the wave functions depending on θ and φ. α_0, γ_0 etc. have only to be replaced respectively by $(\alpha_0)^{v}_{v'}$, $(\gamma_0)^{v}_{v'}$ etc.

Comparison with Experimental Results.—The more important conclusions of the above theory will now be serially stated and compared with experimental results in gases wherever available.[1]

[1] In certain cases, the conclusions have also been found to hold good in liquids and sometimes solids but these will only be referred to occasionally.

The inferences relate to incident unpolarized light unless otherwise stated. Results relating to rotational as well as vibrational scattering will be dealt with in this section.

1. The depolarization factor of each one of the rotational Raman lines should be $\frac{6}{7}$. Measurements have been made by Bhagavantam in hydrogen and deuterium and the results are given below. There is good agreement between experiment and theory.

TABLE XXXII

Depolarization of the Rotational Raman Lines

Transition J.	$0 \rightleftarrows 2$	$1 \rightarrow 3$	$2 \rightarrow 4$	$3 \rightarrow 5$
Hydrogen	0·85	0·86	0·80	0·82
Deuterium	0·86 0·84	0·84	0·86	..

2. The depolarization factor of any vibrational Raman line should range between 0 and $\frac{6}{7}$. Table XXIX contains the results obtained in a few cases.

3. Use of circularly polarized incident light should give rise to a high reversal factor for depolarized lines ($P = 6$ for rotational lines) and a low reversal factor for well polarized lines. No work has been done in gases but these conclusions are confirmed in liquids.

4. Only molecules which are optically anisotropic may give rise to pure rotational Raman scattering. Increased optical anisotropy should result in an enhanced intensity of the rotational scattering. The fact that methane does not exhibit this type of scattering while O_2, N_2, etc., exhibit the same with moderate intensity and CO_2 and N_2O very strongly, is in entire agreement with this conclusion.

5. Vibrational lines which are perfectly polarized consist of isotropic scattering only and should not be accompanied by rotational lines. The total symmetric vibrational line at 2918 in methane is an example of this type. Vibrational lines which are either composed of anisotropic scattering only or which have a large proportion of it in them, are accompanied by

prominent rotation lines. The line at 3018 ($\varrho = 6/7$) in methane and the line at 4156 ($\varrho = 0{\cdot}13$) in hydrogen are respectively examples of this type. Both these are accompanied by rotational lines.

6. The total intensity of a vibrational line $v \rightarrow v'$, inclusive of all the rotational lines accompanying it, is proportional to $\left|(\alpha_\theta)^v_{v'}\right|^2 + \frac{7}{45}\left|(\gamma_0)^v_{v'}\right|^2$ in the parallel component and $\frac{6}{45}\left|(\gamma_0)^v_{v'}\right|^2$ in the perpendicular component per molecule for large values of J and unpolarized incident light. An individual rotational line $J \rightarrow J'$ has an intensity proportional to $\frac{7}{30}[G^s]^{vJK}_{v'J'K} \cdot \frac{1}{2J+1}$ in the parallel component and $\frac{6}{30}[G^s]^{vJK}_{v'J'K} \cdot \frac{1}{2J+1}$ in the perpendicular component per molecule (see 26 and 29). $[G^s]^{vJK}_{v'J'K} \cdot \frac{1}{2J+1}$ in the above expressions is given by

$$[G^s]^{vJK}_{v'J'K} \cdot \frac{1}{2J+1} = \tfrac{2}{3}\, b^{JK}_{J'K}\left|(\gamma_0)^v_{v'}\right|^2. \quad \quad .. \quad (29)$$

The relative intensities[1] of the various rotation lines will be merely proportional to $\frac{2}{3} b^{JK}_{J'K}$ multiplied by the number of molecules having the rotational quantum number J. The relevant values of $b^{JK}_{J'K}$ obtained from Table XXXI for a linear rotator (K = 0) are given below.

$$b^{J0}_{J0} = \frac{J(J+1)}{(2J-1)(2J+3)}$$

$$b^{J0}_{J\pm1\,0} = 0$$

$$b^{J0}_{J+2\,0} = \frac{3}{2}\,\frac{(J+1)(J+2)}{(2J+1)(2J+3)}$$

$$b^{J0}_{J-2\,0} = \frac{3}{2}\,\frac{J(J-1)}{(2J+1)(2J-1)}.$$

The intensity of rotational lines $J \rightarrow J \pm 1$ vanishes, as may be expected. Only double quantum jumps have accordingly been detected in O_2, N_2, H_2, D_2, etc. The intensity of $J: 0 \rightarrow 0$

[1] The factor $(\nu_0 + \nu_{JJ'})^4$ is omitted as $\nu_{JJ'}$ is usually very small.

vanishes so far as it relates to the anisotropic part. This implies that the intensity of the fine structure component of the vibration line $v \rightarrow v'$ relating to J : 0 → 0 should be composed entirely of isotropic scattering and accordingly should be perfectly polarized. The results obtained by Bhagavantam[1] are not in agreement with this conclusion.

The intensity of a line $J \rightarrow J+2$ accompanying a transition $v \rightarrow v'$ will be proportional to

$$g_J (2J+1) e^{\frac{-BhJ(J+1)}{kT}} \cdot \tfrac{2}{3} \cdot b^{J0}_{J+2\,0} \quad \ldots \quad \ldots \quad (30)$$

On the same scale, the intensity of a line $J \rightarrow J-2$ will be obtained by putting $b^{J0}_{J-2\,0}$ in the place of $b^{J0}_{J+2\,0}$ in the above expression. $(2J+1)$ is the degeneracy of the rotational state J. g_J represents the *a priori* probability factor in respect of the rotational state J. For heteronuclear molecules, no distinction need be made between the even and odd rotational quantum numbers and g_J will accordingly be the same for all levels. For homonuclear molecules, the relative statistical weights of the two types have to be taken into account. These figures are given below for a few cases.[2]

Gas	H_2		D_2		N_2		O_2	
J	odd	even	odd	even	odd	even	odd	even
g_J	3	1	1	2	1	2	1	0

The difference in the statistical weights arises from the fact that the nuclei possess spin moments and gives rise to an alternation in the intensities already referred to (see Plate II). The results calculated in respect of the relative intensities of rotational

[1] Ind. Jour. Phys., 7, 549 (1932).

[2] More comprehensive Tables and a detailed discussion of the phenomenon of alternating intensities in the rotational spectra of homonuclear diatomic molecules are given in a number of other places. For example, reference may be made to Jevons, *Report on Band Spectra of Diatomic Molecules*, 139 (1932).

lines at a temperature of 30° for H_2 and D_2 are given in Tables XXXIII and XXXIV respectively. The intensities observed by Bhagavantam, at temperatures close to this, are also given for comparison.

TABLE XXXIII

Relative Intensities of Rotational Lines in Hydrogen

Transition $J \rightarrow J'$	O Series		Transition $J \rightarrow J'$	S Series	
	Calculated	Observed		Calculated	Observed
$2 \rightarrow 0$	0·12	0·13	$0 \rightarrow 2$	0·67	0·73
$3 \rightarrow 1$	0·12	0·13	$1 \rightarrow 3$	2·05	2·0
$4 \rightarrow 2$	0·006		$2 \rightarrow 4$	0·32	0·31
			$3 \rightarrow 5$	0·23	0·24
			$4 \rightarrow 6$	0·01	

TABLE XXXIV

Relative Intensities of Rotational Lines in Deuterium

Transition $J \rightarrow J'$	O Series		Transition $J \rightarrow J'$	S Series	
	Calculated	Observed		Calculated	Observed
$2 \rightarrow 0$	0·57	0·7	$0 \rightarrow 2$	1·33	1·34
$3 \rightarrow 1$	0·22	0·4	$1 \rightarrow 3$	0·90	0·82
$4 \rightarrow 2$	0·20	0·4	$2 \rightarrow 4$	1·47	1·40
$5 \rightarrow 3$	0·01		$3 \rightarrow 5$	0·41	0·46
			$4 \rightarrow 6$	0·32	0·38
			$5 \rightarrow 7$	0·02	

B is taken as 59·40*c* and 29·916*c* for hydrogen and deuterium respectively. The observed results in certain cases represent the averages of the figures obtained with total scattering, horizontal component alone or the vertical component alone. Since all rotational lines are depolarized to the extent of $\frac{6}{7}$, it is immaterial whether the calculations and observations relate to total scattering or to one of the components. The figures given in the Tables are in respect of the pure rotational scattering. In so far as we are dealing with the relative intensities only, the same

calculations apply to the rotational lines accompanying the vibrational line. In the former case the multiplying factor is $\left[(\gamma_0)^v_v\right]^2$ and in the latter, it is $\left[(\gamma_0)^v_{v'}\right]^2$. Experimental results in respect of the latter are not available.

Trumpy[1] has worked with oxygen and his results are compared with the calculated values in Table XXXV. B for oxygen is taken as 1·436*c* and the results are calculated at 30°C. and reduced to the scale in which the fifth Stokes line is taken as 10. The agreement between the calculated and the observed values is fairly satisfactory.

TABLE XXXV

Relative Intensities of Rotational Lines in Oxygen

$J \rightleftarrows J'$		Experimental		Theoretical	
		Stokes	anti-Stokes	Stokes	anti-Stokes
1	3	..	..	4·2	3·9
3	5	..	..	7·2	6·4
5	7	8·8	6·8	9·3	7·7
7	9	9·7	7·5	10·2	8·1
9	11	10·0	6·8	10·0	7·6
11	13	9·1	5·8	9·0	6·4
13	15	7·2	4·5	7·4	4·9
15	17	6·0	3·2	5·7	3·7
17	19	4·3	..	4·1	..
19	21	2·8	..	2·7	..

7. An intercomparison may also be effected between the vibrational scattering $v \rightarrow v'$ and $\triangle J = 0$ and the various accompanying rotational lines, if we confine ourselves to the anisotropic part (perpendicular component) only. If we replace $b^{J0}_{J+2\,0}$ by b^{J0}_{J0} in (30), we get the expressions appropriate to such calculations. The results are given below in Table XXXVI for hydrogen.

[1] Z. f. Phys., *84*, 282 (1933).

TABLE XXXVI

Relative Intensities of the Rotational Lines and the Fine Structure Components of the Vibrational Line (⊥ *Components only*)

Transition							
v:	$0\to 1$	$0\to 1$	$0\to 1$	$0\to 1$	$0\to 1$	$0\to 1$	$0\to 1$
J:	$0\to 0$	$1\to 1$	$2\to 2$	$3\to 3$	$4\to 4$	$0\to 2$	$1\to 3$
Calculated intensity	0	1·37	0·18	0·13	0·06	0·67	2·05

The relative intensities of $v: 0\to 1$, $J: 1\to 3$ and $v: 0\to 1$, $J: 1\to 1$ should be 3 : 2 according to the above Table. Measurements of Bhagavantam reveal a ratio of 1·3 : 2 for these lines.

8. If we again confine ourselves to the anisotropic scattering only, the aggregate intensity of the Q branch bears a ratio given by (31) to the aggregate intensity of the O and S branches.

$$\frac{\text{Q branch (⊥ Components only)}}{\text{O}+\text{S branches (⊥ Components only)}} = \frac{\sum_J N_J \,.\, \frac{2}{3} b^{J0}_{J0}}{\sum_J N_J \,.\, \frac{2}{3} b^{J0}_{J+2\;0} + \sum_J N_J \,.\, \frac{2}{3} b^{J0}_{J-2\;0}}$$

$$\text{where } N_J = g_J(2J+1)\,e^{\frac{-BhJ(J+1)}{kT}} \qquad .. \quad (31)$$

If the temperature and the value of B are such that the major contribution to the intensity comes from molecules having large values of J, it is easily seen that the ratio in (31) tends to 1 : 3. This is the case with molecules having a comparatively large moment of inertia and high temperatures. In such cases, only a fourth of the total anisotropic scattering is present in the Q branch. This is the limiting value of (31) and is identical with what has already been deduced earlier in this chapter on the basis of the elementary theory. The distribution will, however, be different for molecules with small moments of inertia or at comparatively low temperatures.

9. The aggregate intensity of the anti-Stokes rotational lines to that of the Stokes rotational lines will be given by (32).

$$\frac{\sum_J N_J \,.\, \frac{J(J-1)}{(2J+1)(2J-1)}}{\sum_J N_J \,.\, \frac{(J+1)(J+2)}{(2J+1)(2J+3)}} \qquad .. \qquad .. \quad (32)$$

N_J has the same significance as in (31). In the limiting case of high temperatures or large moments of inertia, the ratio becomes unity. Otherwise, there is a certain asymmetry.

10. For symmetric top molecules,[1] the intensity of the lines $\triangle J = \pm 1$ does not vanish as $K \neq 0$. Amaldi and Placzek[2] have studied the case of ammonia and recorded the transitions $\triangle J = \pm 1$ besides $\triangle J = \pm 2$ in accordance with the theory. The distribution of intensity in the various branches has been shown by these authors to be in qualitative agreement with the above theory.

11. Expression (6) has been found to represent the observed ratios of the Stokes and anti-Stokes lines correctly. Table XXXVII gives the results of Sirkar[3] who worked with carbon tetrachloride.

TABLE XXXVII

Ratio of Intensities of Stokes and anti-Stokes Raman Lines[4]

$\nu_{vv'}$	T	$e^{\frac{h\nu_{vv'}}{kT}}$	$\left(\frac{\nu-\nu_{vv'}}{\nu+\nu_{vv'}}\right)^4 e^{\frac{h\nu_{vv'}}{kT}}$	$\frac{I_S}{I_A}$ observed
456 Cm^{-1}	328	7·37	6·27	6·32
315 „	328	3·97	3·57	3·68

12. For linear molecules, the ratio of the intensity of the vibrational Raman line to that of the exciting line is given by (33).

$$\frac{I_{v \to v'}}{I_{v \to v}} = \frac{h/8\pi^2\nu_{vv'}I\,(\alpha'^2 + \frac{13}{180}\gamma'^2)}{\alpha_0^2 + \frac{13}{180}\gamma_0^2} \quad .. \quad (33)$$

(33) is easily obtained from (21) by separating three-fourths of the anisotropic scattering as rotational Raman scattering.

[1] Although nitric oxide molecule is apparently a linear rotator, the presence of a component of electronic angular momentum along the figure axis puts it under this class of molecules. Transitions corresponding to $\Delta J = \pm 1$ are accordingly observed in this case.

[2] Z. f. Phys., *81*, 259 (1933).

[3] Ind. Jour. Phys., *6*, 295 (1931).

[4] If the theory is assumed to be correct, the observed results may be used to calculate the Boltzmann constant.

(33) refers to unpolarized incident light and Q branches only. It is strictly correct for limiting cases alone. For molecules like H_2 and D_2, having a low moment of inertia, the term involving γ'^2 will be somewhat different. As the anisotropic scattering is usually relatively small in the case of vibrational Raman lines as well as in Rayleigh scattering from diatomic or linear molecules in the gaseous state, (33) will be quite close to the correct expression. The figures obtained by Bhagavantam in a few simple cases are quoted below. They are somewhat approximate but may be taken as giving the order of magnitude correctly.

TABLE XXXVIII

Intensities of Vibrational Raman Lines

Gas	$\nu_{vv'}$	$\frac{h}{8\pi^2\nu_{vv'}I}$	$\frac{I_{0\to 1}}{\text{Rayleigh scattering (Q branches only).}}$	$\frac{\alpha'}{\alpha_0}$
Hydrogen	4156	$1{\cdot}43\times 10^{-2}$	$4{\cdot}2\times 10^{-3}$	0·54
Deuterium	2993	$1{\cdot}00\times 10^{-2}$	$3{\cdot}0\times 10^{-3}$	0·32
Oxygen ..	1557	$0{\cdot}092\times 10^{-2}$	$0{\cdot}3\times 10^{-3}$	0·57
Nitrogen	2331	$0{\cdot}085\times 10^{-2}$	$0{\cdot}2\times 10^{-3}$	0·49

$\frac{\alpha'}{\alpha_0}$, given in the last column, has been calculated with the help of (33) by neglecting the terms involving γ. It gives a measure of the extent to which the mean polarizability of the molecule varies when the nuclear distance is varied. It is interesting to note that the order of magnitude of this quantity is about the same in all the molecules. For example, in hydrogen, the value given for $\frac{\alpha'}{\alpha_0}$ implies a value of $0{\cdot}29\times 10^{-16}$ for $\left(\frac{d\alpha}{dr}\right)_0$. This is obtained by taking $0{\cdot}3976\times 10^{-24}$ and $0{\cdot}75\times 10^{-8}$ respectively for the mean polarizability and the nuclear distance for H_2. For a doubling of the nuclear distance, this would mean that the mean polarizability would become one and a half times, causing a corresponding variation in the refractive index. Although such enormous increase in the nuclear distance may not easily be effected by physical processes,

considerable increases may be introduced by raising the temperature of the gas. Increased temperature will result in increased rotational energy and consequent centrifugal expansion. In fact, it may easily be calculated with the help of the above figures that for an increase of about 300°C., the mean polarizability should be expected to increase by about one part in a thousand. Small as this variation is, it must be capable of being detected by sufficiently accurate methods. It is interesting to note that this surprisingly small dependence of the polarizability on the nuclear distance is responsible for the existence of vibrational Raman scattering.

CHAPTER XII

SYMMETRY, SELECTION RULES AND MOLECULAR OSCILLATIONS

Internal Degrees of Freedom of a Molecule.—In this chapter we shall confine ourselves to transitions in which the vibrational energy of the molecule alone plays a part. All the laws thus derived will also apply to cases where a transfer of other types of energy as well is involved, because the interaction terms are usually small. The molecule may be regarded as a mechanical model in which mass points are located at the various centres of the nuclei and bound to each other through different types of forces. Such a system will obviously possess certain normal modes of vibration, each such mode having a characteristic frequency. Any other conceivable type of oscillation of such a system may be pictured as a suitable combination of some or all of the normal modes. If there are n particles in the model, $3n$ co-ordinates will be required to specify the configuration of the system at any instant of time. If we restrict the centre of gravity of the system from undergoing translation and the system itself from undergoing rotation, only $3n-6$ co-ordinates will be needed. Three of the co-ordinates thus removed refer to the location of the centre of gravity and the other three refer to the position of the principal axes of the system in space.[1] In fact, in investigating the interatomic oscillations of a molecule, we are not interested in these degrees of freedom. The remaining $3n-6$ co-ordinates only correspond to the internal degrees of freedom and relate to the positions of the atoms or mass points relative to each other. Corresponding to each co-ordinate, there is one normal mode of oscillation and we accordingly have $3n-6$ normal modes of internal oscillations in a molecule composed of n atoms. Some of these modes may

[1] In the case of a linear molecule, this number may easily be seen to be 5 and accordingly the total number of internal degrees of freedom is $3n$-5 and not $3n$-6.

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have identical frequencies and will not then be counted as independent. Two or more such modes in respect of which an overlapping occurs constitute a degenerate mode, the degree of degeneracy being equal to the number of modes that have identical frequencies. From the point of view of the subject of molecular spectra and molecular structure, several important problems now arise. Amongst these are an investigation of the nature and number of the normal modes, their exact frequencies, the possibility or otherwise of an energy transition on account of each one of them causing a Raman line or an infra-red absorption, etc. Many early attempts have been made to answer these questions in respect of certain simple molecules but the discovery of the Raman effect and the consequent ease and definiteness with which the vibrational frequencies of even complicated molecules can be measured have brought the above subject much to the fore-front in recent years. Two important characters of the molecule, namely the symmetry possessed by it and the forces that bind the various atoms that comprise it, determine the above features. For a complete solution of the problem, a knowledge of both is necessary. Although considerable uncertainty and difference of opinion exists as regards the latter, the symmetry of any molecule may easily be ascertained as it closely follows the distribution of the nuclei in space. It will be shown in the following sections that much useful information may be derived from a knowledge of the symmetry properties.

Methods of Obtaining the Normal Modes of Vibration and Their Frequencies.—The most straightforward method is to formulate the kinetic and potential energy functions of the system in terms of its co-ordinates and to obtain the normal modes by the usual dynamical methods. If the oscillations are regarded as having infinitesimally small amplitudes in comparison with the nuclear distances, both the potential and kinetic energies may be expressed as functions of quadratic terms only, in the following manner.

$$T = \tfrac{1}{2}\sum_{ij} a_{ij}\dot{q}_i\dot{q}_j\,; \quad V = \tfrac{1}{2}\sum_{ij} b_{ij}q_iq_j \quad \dots \quad \dots \quad (1)$$

The method of deducing the normal modes of oscillation of such

a system is treated in detail in standard works under the theory of vibrations.[1] A solution of the problem rests on our being able to find linear transformations of the type

$$q_i = \sum_k l_{ik} Q_k ,$$

which transform T and V into (1*a*).

$$T = \tfrac{1}{2} \sum_k \dot{Q}_k^2 ; \quad V = \tfrac{1}{2} \sum_k \lambda_k Q_k^2 . \quad .. \quad .. \quad (1a)$$

No cross products exist in (1*a*) and the co-ordinates Q_k thus obtained are called the normal co-ordinates. λ_k's are related to the normal frequencies ν_k of the system as in equation (2).

$$\lambda_k = 4\pi^2 \nu_k^2 . \quad .. \quad .. \quad .. \quad (2)$$

λ_k's are the roots of the determinantal equation (3).

$$| b_{ij} - a_{ij} \lambda | = 0 . \quad .. \quad .. \quad .. \quad (3)$$

A solution of this equation will give the normal frequencies and from an examination of the transformations that have to be performed in order that (1) may be written as (1*a*), the nature of the normal co-ordinates and the manner in which the constituent atoms move in each of the modes may be derived.

Application to Molecules.—The simplest case is that of a diatomic molecule. There is only one internal degree of freedom for such a molecule and choosing q, the change in the equilibrium nuclear distance, as the corresponding co-ordinate, we may express the kinetic and potential energies as

$$T = \tfrac{1}{2} \mu \dot{q}^2 ; \quad V = \tfrac{1}{2} F q^2 . \quad .. \quad .. \quad (4)$$

μ is the reduced mass and F is the restoring force called into play per unit increase in the nuclear distance. (4) is easily put in the form of (1*a*) by making the substitution $q = \mu^{-\frac{1}{2}} Q$ and obtaining (4*a*).

$$T = \tfrac{1}{2} \dot{Q}^2 ; \quad V = \tfrac{1}{2} \frac{F}{\mu} Q^2 . \quad .. \quad .. \quad (4a)$$

The frequency of vibration is now obtained as (5) in accordance with (2).

$$\nu = \frac{1}{2\pi} \sqrt{\frac{F}{\mu}} . \quad .. \quad .. \quad .. \quad (5)$$

[1] See Whittaker, *Analytical dynamics.*

This is a well known and frequently used expression. The normal co-ordinate is such that the motion consists of a to and fro movement of the atoms along the nuclear axis.

We shall consider another simple case, namely that of a molecule in which three identical atoms are situated at the corners of an equilateral triangle. Such a system has three internal degrees of freedom and we accordingly require 3 co-ordinates for describing the system. We shall choose these three as the mutual displacements along the valency bonds and express the kinetic and potential energies by (6) and (7) respectively.

$$T = \frac{m}{2}\left\{\tfrac{5}{9}\left(\dot{q}_1^2+\dot{q}_2^2+\dot{q}_3^2\right) - \tfrac{2}{9}\left(\dot{q}_1\dot{q}_2+\dot{q}_2\dot{q}_3+\dot{q}_3\dot{q}_1\right)\right\} \quad \ldots \quad (6)$$

$$V = \frac{F}{2}\left(q_1^2+q_2^2+q_3^2\right). \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (7)$$

The kinetic energy function is obtained in the following manner. It may easily be shown that the symmetry of the configuration demands that the coefficients of $\dot{q}_1^2$, $\dot{q}_2^2$ and $\dot{q}_3^2$ should all be equal and each of these may be represented by A. Similarly, the coefficients of $\dot{q}_1\dot{q}_2$, $\dot{q}_2\dot{q}_3$ and $\dot{q}_3\dot{q}_1$ should all be equal and each of these may be represented by B. Suitable displacements are then given to the atoms subject to the condition that there is no translation or rotation of the molecule as a whole and the kinetic energy is evaluated in each case. By forming a set of equations in this manner, the values of the coefficients A and B, occurring in the function, may be arrived at. The form of the potential energy function given in (7) is of a very simple type and assumes that V depends only on the mutual distances between the constituent atoms. m is the mass of each one of the atoms and F has the same significance as before. The determinantal equation (3) may now be written out and rearranged to give (8).

$$\left(\lambda - \frac{3F}{2m}\right)^2\left(\lambda - \frac{3F}{m}\right) = 0. \quad \ldots \quad \ldots \quad (8)$$

This system has therefore two independent frequencies ν_1 and ν_2 whose values are given by

$$\nu_1 = \frac{1}{2\pi}\sqrt{\frac{3F}{m}}; \quad \nu_2 = \frac{1}{2\pi}\sqrt{\frac{3F}{2m}}.$$

ν_2 is degenerate and involves in it, two normal modes which have identical frequencies. The former corresponds to a mode in which the three atoms move in and out along the radial lines. The latter corresponds to an isotropic motion of the three atoms in the plane of the triangle, each one describing a small circle round its mean position.

Such calculations have been extended by Dennison[1] and others to a number of simple models such as the tetrahedral and the pyramidal molecules but the treatment becomes very laborious even in comparatively less complicated molecules. If we are not particular of evaluating the exact frequencies but only desire to arrive at the number and nature of the normal modes, many short cuts are available[2] and we shall briefly review here the method of extreme force fields developed by Dennison. In this method, different parts of the molecule are first treated as separate units by postulating special types of forces. The characters of the actual case, which are usually intermediate between those of the extremes, are easily deduced from the above results. As an example, we may cite here the case of a pyramidal molecule YX_3, the three X atoms being at the corners of an equilateral triangle which forms the base of the pyramid. Y is at the apex of the pyramid. The group of X atoms may be regarded as one unit and it will accordingly give rise to its internal vibrations. An investigation of these has already been made and it was shown that they were two in number. In each one of these, the atom at the apex will move only slightly and in such a manner as to satisfy the conditions that the centre of gravity of the system shall be fixed and that the molecule as a whole shall not rotate. In the former, the Y atom will move along the axis of the pyramid and the mode will be single. In the latter, the movements of the X atoms are isotropic in the plane and accordingly the Y atom will also move in an isotropic manner in a plane perpendicular to the axis. This mode will, as before, be doubly degenerate. There will

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[1] Astrophys. Jour., *62*, 84 (1925) and Phil. Mag., *1*, 195 (1926).

[2] See R. Mecke, *The Structure of Molecules*, *Leipziger Vortrage* (Eng. Trans.) 23 (1932). D. M. Dennison, Rev. Mod. Phys., *3*, 280 (1931).

be two more oscillations which are similar in character but obtained by reversing the phase of the motion of the triangular base in so far as its internal oscillations are concerned. In one of them, which is single, the motion of the Y atom is still along the axis and in the other, which is doubly degenerate, the motion is in the plane perpendicular to the axis. There are thus altogether two doubly degenerate and two single vibrations for this type of molecule. The directions of motion of each of the atoms may easily be put down for either of the extreme cases, namely, that in which the force between any two of the X atoms is very strong, whereas the force between the Y and any of the X atoms is very weak, and another in which the situation is just the reverse. An actual case will be intermediate between these. For a pictorial representation of these modes, reference may be made to the original paper of Dennison.

Symmetry of a Molecule and its Normal Modes of Oscillation.—It has already been remarked that the application of the above methods to complicated molecules involves practical difficulties. Recent advances in this subject have, however, been made possible by the application of a very different branch of mathematics, namely, the theory of groups. Wigner[1] has shown that such an application greatly facilitates the work with regard to the obtaining of the number and symmetry of the normal modes of oscillation of a molecule. This work has been followed up in a more extensive manner by Tisza,[2] Wilson,[3] Placzek[4] and Rosenthal and Murphy[5]. Placzek has given a number of Tables relating to the symmetry properties and selection rules in respect of the normal modes of various types of molecules. Wilson has dealt with many crystallographic and non-crystallographic groups. Numerous applications to actual cases have subsequently been made by other investigators and a correlation of the conclusions with the experimental results in infra-red absorption and Raman spectra has yielded most

[1] Göttinger Nachrichten, 133 (1930).
[2] Z. f. Phys., *82*, 48 (1933).
[3] Phys. Rev., *45*, 706 (1934) and Jour. Chem. Phys., *2*, 432 (1934).
[4] Handbuch Der Radiologie, *6*, part 2, 205 (1934).
[5] Rev. Mod. Phys., *8*, 317 (1936).

fruitful results from the point of view of structural chemistry. We shall now briefly enunciate the principles underlying this method and outline the main theorems.[1] Every molecule, by virtue of its symmetry, is characterized by a set of symmetry operations which have the property of transforming the molecule into itself. Symmetry operations that are usually met with are rotations about symmetry axes, reflections in symmetry planes, inversion through a centre of symmetry and rotations accompanied by reflection in a plane perpendicular to the axis of rotation. The corresponding symmetry elements that the molecule may be said to possess are an axis of symmetry, a plane of symmetry, a centre of symmetry and a rotation-reflection axis of symmetry respectively. The symbols C_p, σ, i and S_p may be taken to denote respectively a p-gonal axis of symmetry, a plane of symmetry, a centre of symmetry and a p-gonal rotation-reflection axis of symmetry. The set of such operations for a molecule satisfies the requirements noted in Appendix VI and constitutes a *point group.*

The kinetic and potential energies of a molecule, in terms of its normal co-ordinates, are given by (1a). Since the application of a symmetry operation appropriate to the point group of the molecule transforms it into itself, the kinetic and potential energies given by (1a) should be invariant under all such operations. The choice of the normal co-ordinates is accordingly subject to this condition. The most obvious transformations in the normal co-ordinates which satisfy the above requirements are (9) and (10).

$$RQ_k \rightarrow Q_k \quad \ldots \quad \ldots \quad \ldots \quad (9)$$

$$RQ_k \rightarrow -Q_k \quad \ldots \quad \ldots \quad \ldots \quad (10)$$

R denotes a symmetry operation. When it is made to operate on Q_k, the result in the first case is that Q_k remains unchanged whereas in the second case, while its magnitude remains unchanged, the sign changes. The normal co-ordinate Q_k is said to be symmetric with respect to R in the first case and anti-symmetric with respect to R in the second case. In both cases,

[1] For a more detailed treatment, this section should be read in conjunction with Appendices VI and VII.

the energy function is invariant as it involves only the quadratic terms. These relationships hold good, only when the coefficient λ_k of Q_k is different from all the other λ's. In case a degeneracy occurs, more than one Q_k have the same λ as their coefficients and under such conditions it may be shown that the energy functions will remain invariant only when the symmetry operation on any one of the degenerate co-ordinates transforms it into a linear combination of all the degenerate Q's in accordance with (11).

$$RQ_k \rightarrow \sum_n a_{kn} Q_n . \quad \ldots \quad \ldots \quad (11)$$

The summation extends over all the Q's that have the same λ as their coefficients. All the normal co-ordinates Q which transform in accordance with (11) are said to be degenerate. If they are f in number, we have a f-fold matrix (a_{kn}) and the sum of the diagonal components a_{kk} in this transformation is called the character of the symmetry operation R. Denoting this by $\chi(R)$, we have

$$\chi(R) = \sum_k a_{kk} . \quad \ldots \quad \ldots \quad \ldots \quad (12)$$

$\chi(R)$ is given by (12) and we shall have occasion to use this later. It is easily seen that the character of a symmetry operation is $+1$ or -1 according as the normal co-ordinate is symmetric or anti-symmetric with respect to it. The conditions imposed by (9), (10) and (11) restrict the normal modes of oscillation of a molecule. Every mode must come under one or other of these types and they may be classed as symmetric, anti-symmetric or degenerate [1] with respect to each symmetry operation according as the relevant normal co-ordinate transforms as in (9), (10) or (11) respectively, as a result of the symmetry operation. Associated with a given point group, there will be a certain number of symmetry operations and if we consider the possibility of choosing normal co-ordinates which are either symmetric, anti-symmetric or degenerate with respect to each one of these operations, it appears at first sight that many alternatives will

[1] Degeneracy occurs only when there are present either rotation axes or rotation reflection axes of at least trigonal symmetry.

result. Group theory, however, further restricts the normal modes. It may be proved that associated with every group, there is a certain number of *irreducible representations* each of which represents a type of symmetry allowed for a normal co-ordinate. Every normal co-ordinate of a given molecule with a certain point group must possess symmetry characters which come under one or other of these irreducible representations (see Appendix VI). There may, however, be more than one normal co-ordinate associated with each irreducible representation as is often the case. The problem of finding the number and symmetry characters of the normal modes of oscillation of a given molecule, therefore reduces itself to identifying its point group, symmetry operations and irreducible representations and then finding out how many normal modes are associated with each irreducible representation. The method of doing this is dealt with in detail in Appendix VII and the empirical side of it will be clear when we come to consider some examples in a following chapter. The total number should come out as $3n-6$ for a general polyatomic molecule consisting of n atoms and $3n-5$ for a linear molecule after subtracting the modes appropriate to pure translations and rotations.

The questions, as to how many of these will appear in Raman effect alone and with what polarization characters, how many in infra-red, how many in both, and how many in neither are matters for further investigation on the basis of the selection rules. The important theorems, with the help of which the above results may be deduced, are given in Appendix VII. Tables giving the symmetry operations and irreducible representations appropriate to all the crystallographic point groups have been published by Wigner. Tisza has extended these Tables to several non-crystallographic point groups as well. With the help of these Tables, it is now a matter of routine to investigate the number and symmetry properties of the normal modes of oscillation of a given molecular model.

Irreducible Representations and Selection Rules in Respect of Different Point Groups.—Below are given the character Tables,

due to Tisza, in respect of various point groups. For more extensive Tables, drawn up individually for each crystal system, reference may be made to Placzek's paper. Below each Table are given the rules regarding the activity of the normal modes, confining only to the fundamental tones. In the case of the groups derived by combining two groups, the selection rules can be easily arrived at by considering the rules that are appropriate to both the groups or by applying the general formulae given in Appendix VII. Out of the 32 crystallographic point groups, character Tables in respect of 21 groups may be obtained from the Tables given here. The Table given under item 1 contains the groups C_i, C_s and C_2. The Table in respect of C_{2h} may be derived with the help of the relation $C_{2h} = C_2 \times C_i$. The Table given under item 3(*a*) contains the groups C_{3v} and D_3. Tables in respect of D_{3d} and D_{3h} may be derived with the help of the relations $D_{3d} = C_{3v} \times C_i$ and $D_{3h} = D_3 \times C_s$. The Table given under 3(*b*) contains C_{2v}, C_{4v}, C_{6v}, D_2 (V), D_4, D_6 and V_d. Tables in respect of the groups D_{2h} (V_h), D_{4h} and D_{6h} may be derived with the help of the relations $D_{2h} = V \times C_i$, $D_{4h} = D_4 \times C_i$ and $D_{6h} = D_6 \times C_i$. Table given under 4 contains O and T_d. The Table in respect of O_h may be derived with the help of the relation $O_h = O \times C_i$. The triclinic group C_1, having no elements of symmetry, is not considered and ten other groups, S_4, C_4, C_{4h}, T, T_h, C_3, C_{3i}, C_{3h}, C_6 and C_{6h} involving complex representations are omitted.[1] This list completes the crystallographic groups. With the help of the Tables given here, several other non-crystallographic groups also may be dealt with. The notation used is that of Schoenflies.[2] Significance of certain other symbols employed is given below.

E—Identity.

$C_\infty(\varphi)$ written as $C(\varphi)$ .. rotation about an axis of φ.

$2C_\infty(\varphi)$,, ,, $2C(\varphi)$,, ,, $\pm\varphi$.

---

[1] See Wigner, Göttinger Nachrichten, 133 (1930) for these groups.

[2] See Wyckoff, *The Structure of Crystals*, 2nd Edn., 22 (1931).

C_p^k written as C^k .. rotation about a p-fold axis of $k\frac{2\pi}{p}$.

$2C_p^k$,, ,, $2C^k$,, ,, $\pm k\frac{2\pi}{p}$.

S_p^k ,, ,, S^k .. rotation about a p-fold rotation-reflection axis of $k\frac{2\pi}{p}$.

$2S_p^k$,, ,, $2S^k$ .. rotation about a p-fold rotation-reflection axis of $\pm k\frac{2\pi}{p}$.

σ_h . . . reflection plane perpendicular to an axis.

σ_v . . . ,, ,, containing an axis.

In some of the character Tables, a slightly different notation, already described, is sometimes adopted but the meaning is evident. C_p and S_p stand respectively for a p-gonal rotation axis and a p-gonal rotation-reflection axis. Non-degenerate modes are denoted by the letters A, B, etc., doubly degenerate ones by E and the triply degenerate ones by F. M denotes the electric moment vector and its presence in a certain representation denoted by the symbol $\sim$, means that all the normal oscillations coming under that representation are infra-red active. α denotes the polarizability tensor and has the same significance in respect of Raman effect.

1.

C_i		E	i
	C_s	E	σ
A_g	A'	1	1
A_u	A''	1	-1

C_i :—$M \sim A_u$, $\alpha \sim A_g$.

C_s :—$M_z \sim A''$, $M_x \sim A'$, $M_y \sim A'$.

$\alpha_{ii} \sim A'$, $\alpha_{xy} \sim A'$, $\alpha_{xz} \sim A''$, $\alpha_{yz} \sim A''$.

2.

D_∞	E	$2\,C(\varphi)$	C_2
$C_{\infty v}$	E	$2\,C(\varphi)$	σ_v
A_1	1	1	1
A_2	1	1	-1
E_1	2	$2\cos\varphi$	0
E_2	2	$2\cos\varphi$	0
....	....	....	....
E_l	2	$2\cos l\varphi$	0

$M_z \sim \begin{cases} A_1 \text{ for } C_{\infty v} \\ A_2 \text{ for } D_\infty \end{cases}$ $\quad M_\perp \sim E_1$ for both groups.

$\alpha_{zz} \sim A_1,\ \alpha_{xx}+\alpha_{yy} \sim A_1,\ (\alpha_{xz}, \alpha_{yz}) \sim E_1,\ (\alpha_{xx}-\alpha_{yy}, \alpha_{xy}) \sim E_2.$

3. (*a*) p-odd: ω stands for $\frac{2\pi}{p}$ in this Table.

D_p	E	$2C^1$	$2C^{\frac{p-1}{2}}$	pC_2
C_{pv}	E	$2C^1$	$2C^{\frac{p-1}{2}}$	$p\sigma_v$
A_1	1	1	1	1
A_2	1	1	1	-1
E_1	2	$2\cos\omega$	$2\cos\frac{p-1}{2}\omega$	0
E_2	2	$2\cos 2\omega$	$2\cos(p-1)\omega$	0
—	—	—	—	—
$E_{\frac{p-1}{2}}$	2	$2\cos\frac{p-1}{2}\omega$	$2\cos\left(\frac{p-1}{2}\right)^2\omega$	0

The same selection rules as are given for $C_{\infty v}$ and D_∞ apply to these cases also. It may be noted that when $p = 3$; $E_2 = E_1$ and the selection rule for E_1 will include that for E_2 also.

(b) p-even: ω stands for $\frac{2\pi}{p}$ in this Table.

D_p	E	$2C^1$	$C^{\frac{p}{2}}$	$\frac{p}{2}C_2$	$\frac{p}{2}C_2'$
C_{pv}	E	$2C^1$	$C^{\frac{p}{2}}$	$\frac{p}{2}\sigma_v$	$\frac{p}{2}\sigma_v'$
S_{pv}	E	$2S^1$	$S^{\frac{p}{2}}$	$\frac{p}{2}\sigma_v$	$\frac{p}{2}C_2$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
B_1	1	-1	$(-1)^{\frac{p}{2}}$	1	-1
B_2	1	-1	$(-1)^{\frac{p}{2}}$	-1	1
E_1	2	$2\cos\omega$	$2\cos\frac{p}{2}\omega$	0	0
E_2	2	$2\cos 2\omega$	$2\cos p\omega$	0	0
—	—	—	—	—	—
$E_{\frac{p}{2}-1}$	2	$2\cos\left(\frac{p}{2}-1\right)\omega$	$2\cos\frac{p}{2}\left(\frac{p}{2}-1\right)\omega$	0	0

The dashed letters represent a class of symmetry operations which is different from that represented by the undashed letters.

It may be noted that $E_{\frac{p}{2}} = B_1+B_2$. For C_{pv} and D_p, the same selection rules as for $C_{\infty v}$ and D_∞ apply. Special attention may be drawn to the fact that when $p = 4$; $E_2 = B_1+B_2$ and accordingly the rule $(\alpha_{xx}-\alpha_{yy}, \alpha_{xy}) \sim E_2$ splits up into two as $\alpha_{xx}-\alpha_{yy} \sim B_1$ and $\alpha_{xy} \sim B_2$. Similarly for $p = 2$; $E_1 = B_1+B_2$ and the rules $(\alpha_{xz}, \alpha_{yz}) \sim E_1$ and $M_\perp \sim E_1$ split up respectively as $\alpha_{xz} \sim B_1$, $\alpha_{yz} \sim B_2$ and $M_y \sim B_1$, $M_x \sim B_2$. The selection rules for S_{pv} are

$$M_z \sim B_1, \; M_\perp \sim E_1,$$
$$\alpha_{zz} \sim A_1, \; \alpha_{xx}+\alpha_{yy} \sim A_1, \; (\alpha_{xz}, \alpha_{yz}) \sim E_{\frac{p}{2}-1},$$
$$(\alpha_{xx}-\alpha_{yy}, \alpha_{xy}) \sim E_2.$$

In this case also, a splitting of the selection rules occurs when $p \overline{\gtrless} 6$ and this must be taken account of in applying them to actual cases.

4.

O	E	$8C_3$	$3C_2$	$6C_2$	$6C_4$
T_d	E	$8C_3$	$3C_2$	6σ	$6S_4$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
F_1	3	0	-1	-1	1
F_2	3	0	-1	1	-1

$M \sim F_1$ for O; $M \sim F_2$ for T_d.

$\alpha \sim A_1 + E + F_2$ for both groups.

CHAPTER XIII

RAMAN EFFECT AND MOLECULAR STRUCTURE

Notation.—We shall now proceed to consider specific cases of molecules. The choice of these is not exhaustive but the list only represents the more common ones. U_R in the Tables stands for the number of atoms whose positions remain invariant under the symmetry operation. P and D signify a well-polarized and a depolarized Raman line respectively. *f* denotes that the line is forbidden to appear. These characters refer only to the fundamental tones and not to the overtones or combinations. h_j represents the number of group elements under the class j. χ_j' is the character of the operation in question in the representation defined by the cartesian co-ordinates and is equal to $U_R\ (\pm 1+2\cos\varphi_R)$, the + or the − sign being used according as the operation is a pure rotation through φ or a rotation through φ accompanied by a reflection. ψ_j' is the character obtained after allowing for pure rotations and translations and is equal to $(U_R-2)\,(1+2\cos\varphi_R)$ for pure rotations and $U_R\,(-1+2\cos\varphi_R)$ for rotations accompanied by reflections. The number of modes n_i under each representation obtained with the help of the relation (1*a*) of Appendix VII includes the pure rotations and translations, whereas n_i' obtained with the help of the relation (1*b*) excludes the pure rotations and translations.

Diatomic Molecules.—Amongst the diatomic molecules studied are H_2, D_2, N_2, O_2, Cl_2, HCl, HBr, HI, CO and NO. In all these cases, we should expect only one oscillation frequency and the value obtained from the Raman spectra in each case is given below. The restoring force F, expressed as dynes per cm. extension and calculated with the help of the equation $\nu=\frac{1}{2\pi}\sqrt{\frac{F}{\mu}}$, is also given.

	H_2	D_2	N_2	O_2	Cl_2	HCl	HBr	HI	CO	NO
Gas ..	4156	2993	2331	1556	..	2880	2558	2233	2146	1877
Liquid ..	4158	..	2330	1552	555	2778	2487	..	..	..
$F\times 10^{-5}$	5·09	5·28	22·4	11·4	3·22	4·76	3·81	2·92	18·6	15·5

The existence of a dipole moment for HCl and HBr is presumably responsible for the fact that these molecules in the liquid state exhibit frequencies appreciably smaller than those in the gaseous state. F is a measure of the binding strength and the fact that the values may be roughly classified under three ranges in the neighbourhood of 5, 10 and 15 may be noted. This result will be referred to again under the section on valency.

Triatomic Molecules.—There are three different types of practical interest under this class, namely linear symmetrical, linear unsymmetrical and bent symmetrical. The molecules studied under each type and the Raman frequencies obtained in each case are given in Table XXXIX. The frequencies which are given in italics do not represent the fundamentals.

TABLE XXXIX

Raman Frequencies Obtained in Triatomic Molecules

Type	Molecule	Frequencies						
Linear symmetrical	CO_2	*1265*	*1286*	1389	*1409*			
	CS_2	400	*647*	655	*799*	*811*		
Linear unsymmetrical	HCN	..	*2062*	2094			3213	
	COS	524	*(678)*	859	*1041*	*1383*	2055	*2233*
	ClCN	397		729			2201	
	BrCN	368		580			2187	
	ICN	321		470			2158	
	N_2O	..		1285			2224	
Bent symmetrical	H_2O	1665	*3231*	*3436*		3605	..	
	SO_2	525				1145	1334	
	D_2O	1250	*2363*	*2515*		2662	..	
	H_2S	..				2615	..	

The linear unsymmetrical molecules come under the point group $C_{\infty v}$. A marked feature of this group is the absence of a centre of symmetry. The selection rules for this group are

Infra-red active → A_1 and E_1,

Raman active → A_1 and E_1.

E_2 and other representations merge into E_1. Accordingly, all the three fundamental modes should appear in Raman effect as

well as in infra-red absorption. This conclusion is very different from what is expected of symmetrical molecules like CO_2 and CS_2. One of the three modes comes under the class E_1 and is degenerate and should accordingly be depolarized to the limit, while the other two coming under A_1 should be well polarized. We accordingly obtain three Raman lines in ClCN, BrCN and ICN. The three fundamental frequencies of N_2O are 2224, 1285 and 589. All three appear in the infra-red absorption and two of them, namely 2224 and 1285, appear in the Raman effect. 589 has, however, not been recorded but should be present. 1285 has been found to be strongly polarized. This represents an oscillation in which the two outer atoms move in and out. The fact that it is infra-red active is most significant. These results lend strong support to the proposed unsymmetrical structure N-N-O for this molecule. In fact, this structure was first arrived at from the above considerations. Similarly, the third line in HCN should be present at about 712 but is presumably too weak. In COS, several lines other than the three fundamentals are recorded and these have to be explained as overtones or combinations. The weak line at 2062 in hydrocyanic acid is of special significance and has been attributed to the presence of a small percentage of the isomeric form $H-N \equiv C$.

The point group of the symmetrical molecules is $D_{\infty h}$ and differs from $C_{\infty v}$ in having an additional centre of symmetry. Accordingly A_1 and E_1 split up into A_{1g}, A_{1u} and E_{1g}, E_{1u} respectively. The suffixes g and u indicate that the normal co-ordinate is symmetric and anti-symmetric respectively in relation to the centre of symmetry. The selection rules for this group will be those of $C_{\infty v}$ and C_i taken together. These are

$$\text{Infra-red active} \rightarrow A_{1u} \text{ and } E_{1u},$$

$$\text{Raman active} \rightarrow A_{1g} \text{ and } E_{1g}.$$

We at once see that for this group of molecules, none of the lines which appear in the Raman effect should appear in infra-red absorption and *vice versa*. This result is wholly different from what has been obtained for N_2O and may, in fact, be regarded as a criterion for the symmetrical distribution of atoms

in a linear molecule. Of the three fundamental frequencies for CO_2 and CS_2, only one belongs to the class A_{1g}. This is accordingly single, and should give rise to an intense and well-polarized Raman line which is not represented in the infra-red absorption. This mode is the total symmetric one and corresponds to a symmetrical to and fro movement of the outer atoms. One other frequency is of the A_{1u} type and is accordingly only infra-red active. The third one is degenerate and comes under the class E_{1u} arising out of a transverse motion of the central atom. This also does not appear in Raman effect.[1] The detailed correlation of the Raman and infra-red spectra of these molecules has been given in Table XXII.

Symmetrical bent structures of triatomic molecules like H_2O, D_2O, SO_2, H_2S, etc., come under the point group C_{2v}. The character Table and the numbers n_i', etc., for each irreducible representation Γ_i, are given in Table XL.

TABLE XL

Normal Modes of SO_2, etc.

C_{2v}	E	C^1	σ_v	σ_v'	n_i	R & T	n_i'	Raman	Infra-red
A_1 ..	1	1	1	1	3	1	2	P	$M_z \neq 0$
A_2 ..	1	1	−1	−1	1	1	0	..	..
B_1 ..	1	−1	1	−1	3	2	1	D	$M_x \neq 0$
B_2 ..	1	−1	−1	1	2	2	0	..	..
U_R ..	3	1	3	1					
$h_j \chi_j'$ ..	9	−1	3	1					
$h_j \psi_j'$ ..	3	1	3	1					

We see that all such molecules should give rise to three Raman lines all of which are represented in the infra-red absorption. Two of them should be well polarized and the third depolarized to $\frac{6}{7}$. SO_2 accordingly gives three lines at 526,

[1] A faint line corresponding to this at about 400 has been recorded in liquid CS_2. This is presumably due to a distortion of the molecule in the liquid state.

1146 and 1340, all of which are represented in the infra-red absorption. 1340 has been found to be depolarized to the limit. There is some difficulty with regard to H_2O, D_2O and H_2S as the movements of the hydrogen atoms which presumably do not cause appreciable variations in the polarizability tensor give rise to very weak Raman lines. Only two frequencies in H_2O and D_2O and one in H_2S have been recorded. Water gives certain extra bands which have to be ascribed to polymerized molecules and these are given in italics in Table XXXIX.

Molecules of the Type of Phosgene.—The character Table and other particulars in respect of these molecules are given in Table XLI. These are assumed to be plane symmetrical structures possessing the symmetry characters of the point group C_{2v}.

TABLE XLI

Normal Modes of Cl_2CO, etc.

C_2	E	C^1	σ_v	σ_v'	n_i	R & T	n_i'	Raman	Infra-red
A_1 ..	1	1	1	1	4	1	3	P	$M_z \neq 0$
A_2 ..	1	1	−1	−1	1	1	0	..	..
B_1 ..	1	−1	1	−1	4	2	2	D	$M_x \neq 0$
B_2 ..	1	−1	−1	1	3	2	1	D	$M_y \neq 0$
U_R ..	4	2	4	2					
$h_j\chi_j'$ ..	12	−2	4	2					
$h_j\phi_j'$ ..	6	0	4	2					

The Raman spectrum should contain 6 lines, all of which are represented in the infra-red absorption. Three of these should be polarized and three others depolarized to the limit. Table XLII gives the observed frequencies for these molecules. Although the six fundamental frequencies of formaldehyde are known to be 917, 1039, 1460, 1760, 2865 and 2975 from a correlation of various spectra, they are not included in Table XLII as the Raman spectrum is somewhat complicated by the fact that only aqueous solutions of formaldehyde have been studied.

Table XLII*

Raman Frequencies of Cl_2CO, S_2Cl–Cl, $SOCl_2$

Cl_2CO ..	..	301(*m*)	444(*m*)	571(S)	834(*w*)	1810(*m*)
S_2Cl–Cl ..	107(*m*)	210(*m*)	248(*w*)	449(S)	545 (*w*)	..
Cl_2SO ..	193(S)	282(*m*)	343(S)	444(*m*)	488(*m*)	1229(S)

* The last two molecules are provisionally classified here. There is some doubt as regards their structure. The number of lines recorded in S_2Cl_2 is more than what may be expected for the alternative linear symmetrical model. Polarization measurements will be of use in deciding these issues.

Pyramidal Molecules.—Examples under this group are: (*a*) tetratomic pyramidal molecules like ammonia and the trichlorides of P, As, Sb, Bi, etc., and (*b*) molecules of the type XY_3Z such as chloroform, bromoform, methyl chloride, $POCl_3$, etc. In molecules of the latter type, it is assumed that the X and Z atoms are both on the axis of the pyramid whereas the Y atoms are at the corners of its base. All these structures possess the symmetry characters appropriate to the point group C_{3v} and the character Tables and other necessary data for these two types of molecules are given in Tables XLIII and XLIV respectively.

Table XLIII

Normal modes of PCl_3, etc.

C_{3v}	E	$2C^1$	$3\sigma_v$	n_i	R & T	n_i'	Raman	Infra-red
A_1 ..	1	1	1	3	1	2	P	$M_z \neq 0$
A_2	1	1	−1	1	1	0	—	—
E_1 ..	2	−1	0	4	2	2	D	$M_\perp \neq 0$
U_R ..	4	1	2					
$h_j\chi_j'$ ..	12	0	6					
$h_j\psi_j'$ ..	6	0	6					

TABLE XLIV

Normal Modes of $CHCl_3$, etc.

C_{3v}		E	$2C^1$	$3\sigma_v$	n_i	R & T	n_i'	Raman	Infra-red
A_1	..	1	1	1	4	1	3	P	$M_z \neq 0$
A_2	..	1	1	−1	1	1	0	..	..
E_2	..	2	−1	0	5	2	3	D	$M_\perp \neq 0$
U_R	..	5	2	3					
$h_j\chi_j'$	..	15	0	9					
$h_j\psi_j'$	..	9	0	9					

Molecules of type (*a*) should give rise to 4 Raman lines, all of which are represented in the infra-red absorption. Two of these should be well polarized and the other two depolarized to the limit. Trichlorides of phosphorus, arsenic, antimony, etc., and some tribromides have been examined. In all these cases, four Raman lines have been recorded. The results available in respect of their polarization characters show that two of them are well polarized and the other two depolarized to the limit, in accordance with the theory. In the case of ammonia, however, certain complications set in. As the pyramid is probably very flat, one of the frequencies at 950 splits into two. On account of the presence of hydrogen, certain oscillations are very weak.

Molecules of type (*b*) should give rise to 6 Raman lines and show a complete correspondence with the infra-red absorption. Three of these Raman lines should be well polarized and the other three depolarized. Table XLV contains the results obtained in $CHCl_3$, $CHBr_3$ and $POCl_3$ which are typical representatives of this class. Additional lines which are very weak have been recorded in $CHCl_3$ and $CHBr_3$ and these are presumably either overtones or combinations.

TABLE XLV

Raman Frequencies of $CHCl_3$, $CHBr_3$ and $POCl_3$

$CHCl_3$	..	259(S)	364(S)	664(S)	756(*m*)	1214(*w*)	3016(*m*)
$CHBr_3$	..	154(S)	222(S)	538(S)	654(*m*)	1146(*w*)	3023(*m*)
$POCl_3$	..	192(*m*)	268(*w*)	338(*m*)	485(S)	583(*w*)	1290(*w*)

TABLE XLVI

Normal Modes of C_6H_6

	E	$2C^1$	$2C^2$	C^3	$3C_2$	$3C_2'$	i	$2S^2$	$2S^1$	σ_h	$3\sigma_v'$	$3\sigma_v$	n_i	R & T	n_i'	Raman	Infra-red
A_{1g} ..	1	1	1	1	1	1	1	1	1	1	1	1	2	..	2	P	*f*
A_{2g} ..	1	1	1	1	−1	−1	1	1	1	1	−1	−1	2	1	1	*f*	*f*
B_{1g} ..	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1	0	..	0	..	..
B_{2g} ..	1	−1	1	−1	−1	1	1	−1	1	−1	−1	1	2	..	2	*f*	*f*
E_{1g} ..	2	1	−1	−2	0	0	2	1	−1	−2	0	0	2	1	1	D	*f*
E_{2g} ..	2	−1	−1	2	0	0	2	−1	−1	2	0	0	4	..	4	D	*f*
A_{1u} ..	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1	0	..	0	..	..
A_{2u} ..	1	1	1	1	−1	−1	−1	−1	−1	−1	1	1	2	1	1	*f*	$M_z \neq 0$
B_{1u} ..	1	−1	1	−1	1	−1	−1	1	−1	1	−1	1	2	..	2	*f*	*f*
B_{2u} ..	1	−1	1	−1	−1	1	−1	1	−1	1	1	−1	2	..	2	*f*	*f*
E_{1u} ..	2	1	−1	−2	0	0	−2	−1	1	2	0	0	4	1	3	*f*	$M_\perp \neq 0$
E_{2u} ..	2	−1	−1	2	0	0	−2	1	1	−2	0	0	2	..	2	*f*	*f*
U_R ..	12	0	0	0	4	0	0	0	0	12	0	4					
$h_j\,x_j$ ..	36	0	0	0	−12	0	0	0	0	12	0	12					
$h_j\,\psi_j'$ ..	30	−8	0	2	−6	6	0	0	0	12	0	12					

As an illustration of the polarization characters amongst this class of compounds, we may cite here the case of chloroform in which 259, 756 and 1214 are depolarized to the limit whereas the other three, namely 364, 664 and 3016, are well polarized. This is in complete agreement with the theory.

Benzene.—We shall assume a plane regular hexagonal structure for the benzene molecule, the symmetry of which conforms to the point group D_{6h}. The character Table for this has to be derived from that of D_6 with the help of the relation $D_{6h} = D_6 \times C_i$. Every oscillation characteristic of the group D_6 will now split up into two. We shall, as before, distinguish these by the prefixes *g* and *u* according as they are symmetric or anti-symmetric with respect to the centre of symmetry. Table XLVI contains the relevant characters.

The results show that we should expect 2 polarized and 5 depolarized Raman lines, none of which are represented in the infra-red absorption. On the other hand, we should expect 4 infra-red maxima which are not represented in the Raman effect. A detailed comparison of the experimental results in Raman effect and infra-red absorption has already been effected in chapter X, where it was shown that there was no real and significant coincidence between any of the Raman lines and infra-red absorption maxima. The two polarized Raman lines that are to be expected are observed at 992 and 3063. The five depolarized Raman lines are observed at 607, 850, 1181, (1586-1608) and 3046. These results strongly support the hypothesis that the symmetry of the benzene molecule conforms to the point group D_{6h}. Other possible point groups may be considered and shown to lead to results which are in disagreement with the experimental facts. We have accordingly to conclude that the benzene molecule is a plane regular hexagon possessing all the elements of symmetry that are characteristic of the point group D_{6h}.

The Nitrate and the Carbonate Ions.—In these groups, the three oxygen atoms are at the corners of an equilateral triangle and the nitrogen or the carbon atom is at its centre. The symmetry is that of the point group D_{3h}. This group has to be derived from D_3 as before with the help of the relation

$D_{3h} = D_3 \times C_s$. Each one of the normal modes appropriate to D_3 will again split into two. We shall distinguish them by one and two dashes respectively according as they are symmetric or anti-symmetric with respect to the plane of symmetry. BCl_3 is also a plane molecule and has accordingly to be classed under this group. Table XLVII gives the relevant characters.

Table XLVII

Normal Modes of the Nitrate and Carbonate Ions

D_{3h}	E	$2C^1$	$3C_2$	σ_h	$2S^1$	$3\sigma_v$	n_i	R & T	n_i'	Raman	Infra-red
A_1' ..	1	1	1	1	1	1	1	..	1	P	*f*
A_2' ..	1	1	−1	1	1	−1	1	1	0	..	..
E_1' ..	2	−1	0	2	−1	0	3	1	2	D	$M_\perp \neq 0$
A_1'' ..	1	1	1	−1	−1	−1	0	..	0	..	..
A_2'' ..	1	1	−1	−1	−1	1	2	1	1	*f*	$M_z \neq 0$
E_1'' ..	2	−1	0	−2	1	0	1	1	0	..	..
U_R	4	1	2	4	1	2					
$h_j\chi_j'$	12	0	−6	4	−4	6					
$h_j\psi_j'$	6	0	0	4	−4	6					

These models should therefore be expected to give three Raman lines, two of which are depolarized to the limit, the third one being well polarized. The experimental results are in entire agreement with these conclusions as may be seen from Table XXIII. The principal lines at 1050 in NO_3^- and 1088 in CO_3^- have been found to be well polarized. The other two lines in both cases are depolarized and are present also in the infra-red absorption. The frequency corresponding to A_2'' does not appear in Raman effect. Its first overtone has, however, been recorded both for the NO_3 and the CO_3 groups and this is in accordance with the selection rules.

Tetrahedral Molecules.—Examples under this group are: (*a*) pentatomic tetrahedral molecules like the tetrahalogenides of carbon, silicon, tin, titanium, etc., methane, SiH_4, etc., and (*b*) molecules like P_4. In P_4, it is assumed that the atoms are at the

corners of a regular tetrahedron. The point group in both cases is T_d and the character Tables and other features are given in Tables XLVIII and XLIX.

TABLE XLVIII

Normal Modes of CCl_4, etc.

T_d	E	$8C_3$	$3C_2$	6σ	$6S_4$	n_i	R & T	n_i'	Raman	Infra-red
A_1 ..	1	1	1	1	1	1	..	1	P	*f*
A_2 ..	1	1	1	−1	−1	0	..	0	..	..
E ..	2	−1	2	0	0	1	..	1	D	*f*
F_1 ..	3	0	−1	−1	1	1	1	0	..	..
F_2 ..	3	0	−1	1	−1	3	1	2	D	active
U_R ..	5	2	1	3	1					
$h_j\chi_j'$ ..	15	0	−3	18	−6					
$h_j\psi_j'$ ..	9	0	3	18	−6					

TABLE XLIX

Normal Modes of P_4

T_d	E	$8C_3$	$3C_2$	6σ	$6S_4$	n_i	R & T	n_i'	Raman	Infra-red
A_1 ..	1	1	1	1	1	1	..	1	P	*f*
A_2 ..	1	1	1	−1	−1	0	..	0	..	..
E ..	2	−1	2	0	0	1	..	1	D	*f*
F_1 ..	3	0	−1	−1	1	1	1	0	..	..
F_2 ..	3	0	−1	1	−1	2	1	1	D	active
U_R ..	4	1	0	2	0					
$h_j\chi_j'$ ..	12	0	0	12	0					
$h_j\psi_j'$ ..	6	0	6	12	0					

Molecules of Type (*a*) should give four Raman lines, only two of which are represented in the infra-red absorption. One of the four Raman lines should be perfectly polarized while the other three are depolarized to the limit. Several tetrahedral molecules have been studied and in almost all the cases, the

results obtained are in entire agreement with the above conclusion. In certain cases, such as CCl_4, more than four lines have, however, been recorded but alternative and satisfactory explanations based on the special conditions prevailing in the molecules may be given. The observed depolarization of the Rayleigh scattering as well as that of the total symmetric Raman line at 459 in CCl_4 is not in agreement with the conclusions of the theory. A plausible explanation for this result is that we are dealing with the scattering coming from an admixture of isotopic molecules CCl_4^{35}, $CCl_3^{35}Cl^{37}$, $CCl_2^{35}Cl_2^{37}$, $CCl^{35}Cl_3^{37}$ and CCl_4^{37} and not with a single type as has been assumed in the theory. Only the first and the last types in the above series belong to the point group T_d whereas the others may be expected to give rise to slightly depolarized Rayleigh scattering as well as slightly depolarized total symmetric Raman lines. The Raman lines occurring in most of the tetrachlorides have been examined in respect of their polarization characters and similar results recorded. All of them show three lines which are depolarized to the extent of $\frac{6}{7}$ and one strong line exhibiting a small but definite depolarization. Other possible models such as a pyramid or a plane may be considered for these molecules and the results derived shown to be in disagreement with the observed facts.[1]

The case of P_4 coming under type (*b*) of this group is of great interest. The assumed model should give rise to one polarized Raman line and two depolarized Raman lines. The Raman spectrum of phosphorus has been examined both in the solid and the liquid states and three lines have been recorded at 363, 465 and 606. The first two lines have a depolarization factor of 0·86 and the third line is very well polarized.[2] These results are in very good agreement with the conclusions of the theory. The structure proposed is also confirmed from X-ray investigations.

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[1] See Placzek, *Handbuch Der Radiologie*, *6*, part 2, 205 (1934).

[2] This line should be perfectly polarized according to the theory but a small depolarization of 0·05 has been recorded by Venkateswaran, Proc. Ind. Acad. Sci., *4*, 345 (1937). The origin of this is not clear.

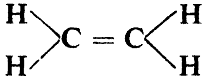
Ethylene.—The structure of this molecule is assumed to be a plane symmetrical one given by . The point group is D_{2h} and has to be derived from D_2 with the help of the relation $D_{2h} = D_2 \times C_i$. Each one of the representations under D_2 will split into two and these may be distinguished as before with the help of the suffixes g and u. The character Table and the results deduced therefrom are given in Table L.

TABLE L

Normal Modes of C_2H_4

D_{2h}	E	C^1	C_2	C_2'	i	σ_h	σ_v	σ_v'	n_i	R & T	n_i'	Raman	Infra-red
A_{1g}	1	1	1	1	1	1	1	1	3	0	3	P	f
A_{2g}	1	1	−1	−1	1	1	−1	−1	1	1	0	..	..
B_{1g}	1	−1	1	−1	1	−1	1	−1	3	1	2	D	f
B_{2g}	1	−1	−1	1	1	−1	−1	1	2	1	1	D	f
A_{1u}	1	1	1	1	−1	−1	−1	−1	1	0	1	f	f
A_{2u}	1	1	−1	−1	−1	−1	1	1	3	1	2	f	$M_z \neq 0$
B_{1u}	1	−1	1	−1	−1	1	−1	1	2	1	1	f	$M_y \neq 0$
B_{2u}	1	−1	−1	1	−1	1	1	−1	3	1	2	f	$M_x \neq 0$
U_R	6	2	0	0	0	0	6	2					
$h_j\chi_j'$	18	−2	0	0	0	0	6	2					
$h_j\psi_j'$	12	0	2	2	0	0	6	2					

Ethylene should accordingly give three polarized and three depolarized Raman lines, none of which are represented in the infra-red absorption. Several authors have discussed the vibrational spectrum of ethylene and concluded that these six Raman active frequencies are probably represented by 1621, 3019, 1344, 3069, 950 and 1100. The first three are the total symmetric oscillations (A_{1g}) and these have been found to be strongly polarized in accordance with the theory. Of the last three, only two have yet been recorded and the third is presumably weak. Other weak lines not represented in the above scheme have also been recorded but these are probably either overtones or forbidden lines, coming out weakly in the liquid

state owing to internal fields slightly distorting the symmetry of the molecule.

Spectra of Molecules having Similar Structures.—The following charts illustrate in a very striking manner, the similarity between the Raman spectra of molecules having similar structures. Figs. 20 and 21 relate respectively to the trichlorides and tetrachlorides that have been studied.

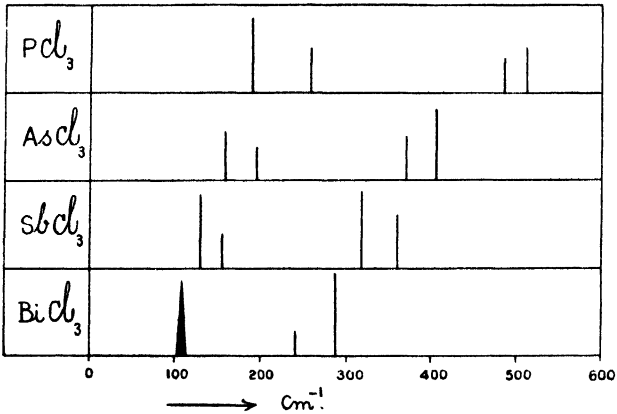


FIG. 20.

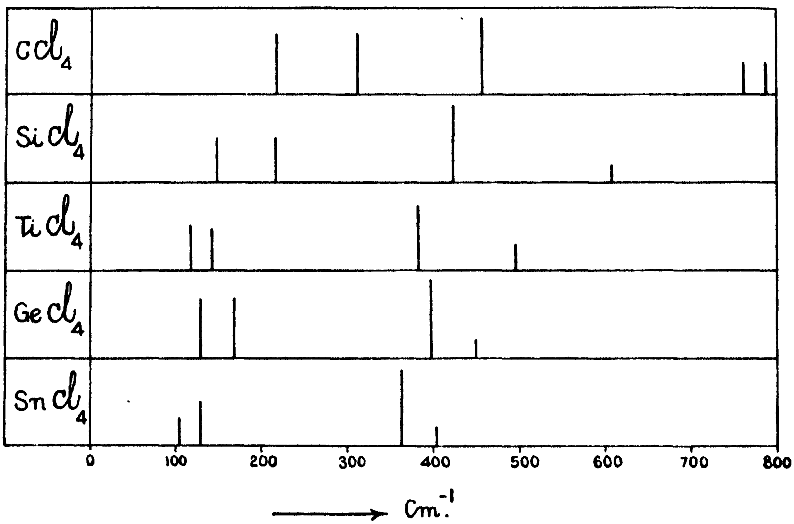


FIG. 21.

The Nature of Interatomic Forces and Evaluation of the Normal Frequencies.—Hitherto we have been concerned only with deriving the number, activity and polarization characters of the normal modes. This information is no doubt very valuable but not complete. It has already been mentioned in the beginning that unless specific types of forces are postulated and the determinantal equation solved, we cannot obtain the frequencies in terms of the masses of the constituent atoms and the binding forces. Much useful work has been done in this direction as well. Several investigators have found that any one type of forces alone is not sufficient to explain the magnitudes of the observed frequencies. Amongst the various types that have been tried are the central forces and the valence forces. Very satisfactory agreement is not obtained in either case. The valence type of force field has, however, been found to be a better approximation than the central force field. Nagendranath [1] has obtained good agreement between the calculated and observed results in some cases by postulating additional forces such as the intravalence forces. Sutherland and Dennison [2] have attempted to express the potential energy of the molecule as the sum of general potential functions of groups of atoms in the molecule together with certain small interaction terms. The potential functions of the groups themselves are derived from their known vibrational frequencies. In this way, they have obtained several interesting results. Van Vleck and Cross [3] have evaluated the potential functions for the H_2O molecule from purely theoretical considerations. Urey and Bradley [4] have also assumed forces perpendicular to the bond lines in addition to the central forces. Manneback and co-workers have made a very extensive study of these problems. From these and many other investigations which are not cited here, it is seen that no single and simple type of force field represents the results with any degree of exactness.

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[1] Ind. Jour. Phys., *8*, 581 (1934) and Proc. Ind. Acad. Sci., *1*, 250 (1934).

[2] Proc. Roy. Soc., *148*, 250 (1935).

[3] Jour. Chem. Phys., *1*, 357 (1933).

[4] Phys. Rev., *38*, 1969 (1931).

CHAPTER XIV

RAMAN EFFECT IN RELATION TO CRYSTAL STRUCTURE

Introduction.—The comparative ease with which experimental data may be collected in liquids has resulted in the accumulation of a wealth of detail relating to this branch. Many gases have also been studied, by employing special technique, on account of their simplicity and theoretical importance. Such studies, which are primarily intended to throw light on problems relating to the structure of molecules, have dominated the field during the past ten years. Similar advance has not been made in the case of solids, as numerous experimental difficulties arise out of the fact that it is not easy to get large and transparent solid lumps or flawless single crystals of appreciable size. A study of the Raman effect in the solid state may proceed in two distinct directions according as we use an aggregate of randomly oriented crystals (crystal powder) or a single crystal as the scattering unit. Some special experimental methods have been evolved for the former case and these are described in the next chapter. The fact that in such a case, we are dealing with a randomly oriented mass makes the situation resemble closely that prevailing in a liquid or a gas and many of the interesting features peculiar to the crystal are missed. Nevertheless, results of great complexity are occasionally obtained in such cases and attempts have been made to correlate these with the internal structure of the crystal without reference to the marked directional properties that are usually characteristic of a single crystal. On the other hand, no special arrangements are necessary for obtaining the Raman spectrum of a single crystal but all the difficulty lies in the direction of securing a properly cut and polished piece of suitable size exhibiting no internal flaws. Once this is achieved, a very wide field of investigation is at once opened up and it may be hoped that such studies will reveal the intimate connection that is likely to

exist between crystal symmetry and light scattering on the one hand and allied optical properties of the crystal on the other.

Advantages of Using a Single Crystal.—From the point of view of light scattering, a single crystal stands on a special footing for the following reasons :—

1. The scattering units (groups of atoms that make up the ions or molecules in the crystal) are oriented in a definite and ascertainable manner with respect to the directions of incidence and observation.

2. Unlike the case of a fluid, where the only possible arrangement of the scattering units is that of the random type, the case of a crystal enables us to obtain a variety of orientations corresponding to different settings of the crystal axes. This results in our obtaining a much wider range of information.

3. Any unit cell in the crystal is exactly like any other and the somewhat complicated problem of studying the dynamics of the whole crystal is, accordingly, simplified to some extent.

A Simple Chain Lattice.—In order to bring out the full significance of the results, it is necessary to obtain a general idea of the dynamics of crystal lattices. This subject has been studied in great detail by Born and Karman and a full account of this theory is given in a number of places.[1] Following Born, we shall start by considering the elementary case of a chain lattice. If we have an infinitely extending chain of atoms as in Fig. 22,

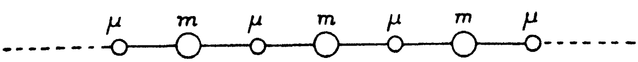


FIG. 22.

and if we assume a harmonic binding between the particles, the equations of motion of the $2n$th and $(2n+1)$th particles may be written as

$$\left.\begin{aligned} m\ddot{U}_{2n} &= \alpha(U_{2n+1}+U_{2n-1}-2U_{2n}) \\ \mu\ddot{U}_{2n+1} &= \alpha(U_{2n+2}+U_{2n}-2U_{2n+1}) \end{aligned}\right\} . \qquad .. \quad (1)$$

It may be noted that all the even numbered atoms have a mass m and the odd numbered ones have a mass μ. U_n represents

[1] *Handbuch Der Physik*, XXIV/2, 638 (1933).

the displacement of the nth atom and α is the restoring force called into play for a unit change in the mutual distance between any two adjacent atoms, the normal value of which is denoted by a. The whole motion of the lattice can be represented by a system of such coupled differential equations. By assuming that the solutions of these equations are periodic in time as well as position, we can write

$$\left.\begin{aligned} U_{2n} &= U' \,.\, e^{i(-\omega t + 2na\tau)} \\ U_{2n+1} &= U'' \,.\, e^{i(-\omega t + \overline{2n+1}a\tau)} \end{aligned}\right\}, \quad \ldots \quad \ldots \quad (2)$$

where $\omega = 2\pi\nu$ and $\tau = \frac{2\pi}{\lambda}$. ω and τ are the important parameters and they respectively define the periodicities in time and in space. ω stands for the number of vibrations in 2π seconds and τ stands for the number of waves contained in a distance of 2π cms., λ being the corresponding wave-length. Combining (2) with (1) so as to eliminate the U's, we obtain the set of equations (3).

$$\left.\begin{aligned} (m\omega^2 - 2\alpha)U' + 2\alpha \cos a\tau \,.\, U'' &= 0 \\ 2\alpha \cos a\tau \,.\, U' + (\mu\omega^2 - 2\alpha)U'' &= 0 \end{aligned}\right\}. \quad \ldots \quad (3)$$

If we neglect the trivial solution $U' = U'' = 0$, we obtain (4).

$$\omega^2 = \frac{\alpha}{m\mu}\left\{m + \mu \pm \sqrt{m^2 + \mu^2 + 2m\mu \cos 2a\tau}\right\}. \quad \ldots \quad (4)$$

Combining (3) and (4), we get (5).

$$\frac{U'}{U''} = \frac{-2\alpha \cos a\tau}{m\omega^2 - 2\alpha} = \frac{-2\mu \cos a\tau}{m - \mu \pm \sqrt{m^2 + \mu^2 + 2m\mu \cos 2a\tau}}. \quad \ldots \quad (5)$$

At this stage we may consider the case in which m and μ are to be regarded as unequal, separately from the one in which the two sets of atoms are to be regarded as having the same mass. In the former, if we assume that $m > \mu$, and plot ω as a function of $a\tau$ in accordance with (4), we obtain the two curves given in Fig. 23a. It is easily seen that the function repeats itself after $a\tau$ becomes $a\tau + \pi$ and hence the graphs are given between the limits $a\tau = -\frac{\pi}{2}$ and $a\tau = \frac{\pi}{2}$ only. The upper curve corresponds to the plus sign and the lower one to the minus sign in (4). For small values of $a\tau$, (4) may be expanded

and written as two separate series corresponding respectively to the two separate curves as follows.

$$\omega_1^2 = 2\alpha \cdot \frac{m+\mu}{m\mu} - (a\tau)^2 \frac{2\alpha}{m+\mu} + \ldots\ldots\ldots$$

$$\omega_2^2 = (a\tau)^2 \frac{2\alpha}{m+\mu} + \ldots\ldots\ldots$$

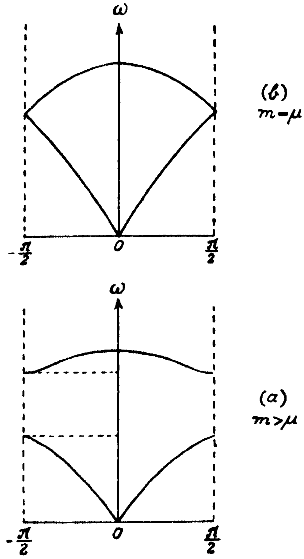


FIG. 23.

As $a\tau \rightarrow 0$ or as $\lambda \rightarrow \infty$, the first series tends to an upper limit given by the peak of the upper curve in Fig. 23*a*, whereas the second series tends to a lower limit of zero given by the depression in the lower curve. It may also be noted that when $a\tau \rightarrow 0$, the plus sign in (5) gives $\frac{U'}{U''} = -\frac{\mu}{m}$ and the minus sign in (5) gives $\frac{U'}{U''} = 1$. Since $\frac{U_{2n}}{U_{2n+1}} = \frac{U'}{U''} \cdot e^{-ia\tau}$, we conclude that the displacements of the neighbouring atoms are in opposite directions in the modes belonging to the first series (ω_1) and that they are in the same direction and differ by infinitesimally small

amounts in the modes belonging to the second series (ω_2). These series have been respectively called the optical and the acoustic series of oscillations. Figs. 24*a* and 24*b* are pictorial

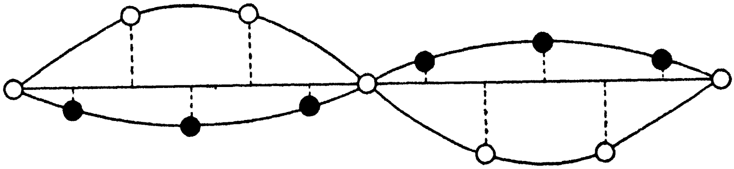


FIG. 24*a*.

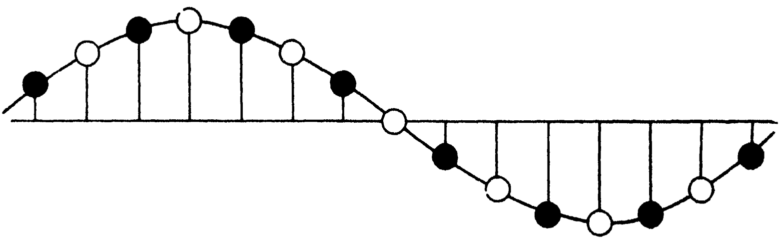


FIG. 24*b*.

representations of these two types of oscillations. It is now not difficult to see that the limiting oscillation ($\lambda \rightarrow \infty$) of the optical series consists of a mutual displacement of the two portions of the lattice against each other, such that the centre of gravity remains undisplaced, whereas the limit of the acoustic series is fundamentally different in that it is a type of translatory motion. In case $m = \mu$, we have (6) instead of (4).

$$\omega^2 = \frac{2\alpha}{m}(1 \pm \cos a\tau) \quad \ldots \quad \ldots \quad (6)$$

Fig. 23*b* represents the two relevant curves. The two series merely merge into each other at the limits $a\tau = \frac{\pi}{2}$ and $a\tau = -\frac{\pi}{2}$.

Three Dimensional Lattices.—By extending these ideas to three dimensional lattices, Born has shown that the normal oscillations of such lattices may similarly be divided into two classes. We also get the result that if there are *n* atoms in each

unit cell,[1] there are $3n$ series on the whole, three of which are of the acoustic type having zero frequencies in the limit and $3n-3$ of which are of the optical type. The distinction between these two types is the same as that deduced in the case of the simple lattice. It may also be shown that, provided the number of atoms is very large, the only oscillations that are of any significance in either absorption or light scattering are the limiting ones. It may be recalled that these limiting ones are characterized by the fact that λ is infinitely large or that a large number of neighbouring atoms move in the same phase. Others are not significant for our purpose and we have accordingly to deal with the $3n$ limits only.

The optical series may further be divided into two classes, namely, those involving relative motions of the ionic or the molecular units as a whole and those involving relative motions also of the atoms that constitute the units. In the former, which may be called the lattice oscillations, the forces are usually weak and the frequencies are relatively small. In the latter, which may be called the internal oscillations, the forces are usually strong and the frequencies are relatively large. Such a distinction is, however, somewhat arbitrary and the two types occasionally run into each other.

When light falls on such a system, the three series of acoustic waves react in a manner which is fundamentally different from that observed in the case of the other $3n-3$ optical series. The presence of such acoustic waves results in a stratification of the medium, giving rise to Brillouin components in the scattered light. An elementary theory of this effect, for a case in which the medium is non-crystalline, i.e., when there is only one sound velocity associated with a specific direction, is given later in this book. In general, however, there are always three distinct sound velocities associated with a given direction in a crystal which generate an acoustic wave surface of three sheets.

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[1] The theory may formally be extended to the case of n particles, covering the nuclei as well as the electrons. If, as has been done here, each nucleus with the electrons belonging to it is regarded as a single particle or atom, we confine ourselves to the infra-red region of the spectrum only.

These should, accordingly, give rise to six Brillouin components, three on each side of the centre or the undisplaced position. Gross[1] reported some preliminary results in crystalline quartz which seemed to reveal the existence of the expected number of Brillouin components. Raman and Venkateswaran[2] have subsequently been able to reproduce an exceptionally striking photograph which they obtained with gypsum showing the six components.

The limits of the $3n-3$ optical series, on the other hand, manifest themselves either directly as absorption bands in the infra-red or indirectly as Raman radiations in the scattered light, the frequency shifts in the latter case corresponding to their respective limits, provided they are permitted to do so by the usual selection rules. As has already been explained, a certain number of these will be classed as lattice lines and the others as internal lines.

In cases where two of the crystal axes become equal, as in a trigonal or a hexagonal crystal, there will be only two distinct degrees of freedom corresponding to the acoustic series limits and $2n-2$ distinct degrees of freedom corresponding to the optical series limits. A two-fold degeneracy sets in for all the oscillations that take place in the symmetry plane. Similarly, in a cubic crystal, a three-fold degeneracy sets in and there are only $n-1$ optical series if there are n atoms in each unit cell. This rapid diminution in the number of distinct normal oscillations of the lattice is the first and the most important consequence of increasing crystal symmetry.

Application to Actual Crystals.—It has been pointed out in chapter II that an ideal crystal, in which thermal motions may be ignored, may not be expected to scatter any light at all. An actual crystal, by virtue of its temperature, is not entirely free from thermal agitation and will accordingly scatter light. The heat content of such a crystal has been pictured in the foregoing paragraphs as equivalent to a system of waves, which will be mostly of the acoustic type at ordinary temperatures.

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[1] Comptes Rendus (Doklady) de l'Acad des Sci., U.S.S.R., *18*, 93 (1938).
[2] Nature, *142*, 250 (1938).

The experimental confirmation of the existence of Brillouin components in the light scattered by crystals may be regarded as a satisfactory proof of the validity of such an analysis. The limiting frequencies of the optical series, which are comparatively high, will manifest themselves in absorption and Raman scattering as induced effects. If we remember that these limiting oscillations are characterized by the fact that a large number of equivalent neighbouring atoms are all moving in the same manner and in the same phase, the problem of analyzing the modes of such oscillations becomes very easy. This situation is alternatively described by saying that all the equivalent points of the lattice have the same motion at a given instant of time. Accordingly, we need consider the group of *n* non-equivalent points which constitute the unit cell of the crystal lattice and describe their positions for completely specifying the motion of the whole lattice. This group may be treated, by applying methods which are exactly similar to those already described in the case of molecules. Several crystals have been dealt with in this manner in a recent paper by Bhagavantam and Venkatarayudu.[1] Some general results only will be quoted here.

When a group of atoms constituting an ion or a molecule forms part of the unit cell of a crystal, its normal modes will in general undergo modification in three directions. The most important modification is in respect of the degenerate modes. They continue to be degenerate in the crystal as well, only when the crystal possesses the same order of symmetry as the free ion or the molecule. If the symmetry breaks down, the degeneracy also breaks down and each degenerate mode will split and give rise to the appropriate number of distinct modes. For example, the SO_4 ion, having a tetrahedral symmetry in the free state, has two triply degenerate and one doubly degenerate normal modes. When a monoclinic $CaSO_4,2H_2O$ crystal (gypsum) or an orthorhombic $CaSO_4$ crystal (anhydrite) is built out of them, each one of the degenerate modes splits into three or two distinct normal modes in the crystal, as the case may be. This kind of

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[1] Proc. Ind. Acad. Sci., *9*, 224 (1939).

splitting may be referred to as splitting due to degradation of symmetry. The separation between the split components may or may not be very prominent.

Apart from this kind of splitting, we may obtain a further multiplication of lines on account of the fact that each unit cell contains more than one ion or molecule, as the case may be. Every normal mode of the free ion, on this score, will be replaced by *m* normal modes in the crystal, if *m* is the number of ions or molecules contained in the unit cell. This situation arises out of the fact that the *m* ions contained in the unit cell, which are not strictly identical with each other in the matter of their environment, may all oscillate in accordance with a particular normal mode, some of them moving in phase and others out of phase and *vice versa*. We get several such possibilities but the frequencies of all these combinations will not be very different from one another, as the coupling forces between various groups are not usually very strong. This kind of splitting, the origin of which may be traced to the environmental changes from one ion to another in the same unit cell of the crystal, will be much less prominent than the splitting due to degradation of symmetry and is likely to be of the same order as the shifts that are usually obtained, with changing concentrations, in certain Raman frequencies due to ions in solution.

The third direction in which changes may occur, as we pass from a free ion to a crystal, is in respect of the selection rules. Very often, at least one component arising from a given Raman active mode of the free ion will be Raman active in the crystal and conversely, every Raman active mode of the crystal would have arisen from one or other such modes of the free ion. Exceptions may occur and an example is the line at 852 appearing in the Raman spectrum of aragonite and arising from an inactive mode of the free CO_3 ion.

Thus the Raman spectrum of a crystal need not be identical with that obtained either in the molten or in the dissolved state of the same substance but may differ in one or all of the following respects. Some of the lines may split into close components, additional lines may appear and some of the lines may disappear in the crystal. It may, nevertheless, be noted that the

splitting is usually very small and that the latter phenomena are of infrequent occurrence. This explains the general similarity that has frequently been noticed in the literature between the Raman spectra of crystals and the corresponding melts or solutions.

Some Cases of Special Importance.—Diamond and rock salt crystals will now be considered in some detail. They belong to the cubic system and their structures represent two typical classes. Special interest also attaches to these two substances, as their Raman spectra have been studied with great care by a number of investigators. Fig. 25*a* represents a unit cell of the diamond lattice and Fig. 25*b* represents a unit cell of the rock salt lattice. In both cases, there are only two non-equivalent atoms in each cell and on account of cubic symmetry, we should expect only one triply degenerate normal oscillation of the optical type for each one of these lattices. In the case of

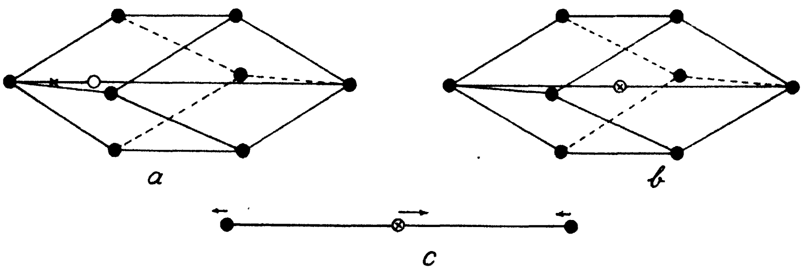


FIG. 25.

diamond, this may be pictured as a to and fro motion, against each other, of the two interpenetrating lattices. In the case of rock salt, one portion of the lattice, consisting of the sodium atoms alone, oscillates against the other, consisting of the chlorine atoms. The location of the centre of symmetry is different in the two cases and this results in the normal oscillation becoming symmetric with respect to the centre in diamond and anti-symmetric with respect to it in rock salt. We should accordingly expect a strong Raman line in diamond with no corresponding absorption in the infra-red and a strong infra-red absorption in rock salt with no corresponding Raman line. It is now well

known that the experimental results are in full agreement with these conclusions.

A better physical picture of this interesting difference between the two types of crystals may be obtained by referring to Fig. 25. In *a* (diamond), all atoms denoted by dots are equivalent and belong to one lattice and that denoted by a circle belongs to the other. The location of the centre of symmetry is shown by the cross and it is easily seen that a mutual oscillation of the two lattices, which is symmetric with respect to the centre, resembles the only normal oscillation of a diatomic molecule and is accordingly Raman active. In *b* (rock salt), same notation is employed and it is easily seen that the location of the centre is such that the normal oscillation is anti-symmetric with respect to it. This resembles one of the normal modes of a linear symmetrical triatomic molecule, shown in *c*, and is accordingly Raman inactive and infra-red active. Crystals like those of KCl, KBr, etc., which have the NaCl structures will be expected to behave similarly and exhibit no Raman lines, whereas crystals of ZnS, AgI and all others having the diamond arrangement may be expected to behave like diamond.

Another interesting feature about diamond, which may be mentioned here, is the fact that while the transverse Rayleigh scattering in it should be perfectly polarized, the Raman line should be expected to exhibit an appreciable depolarization, because it comes under the degenerate class. This statement applies to all cubic crystals, provided the normal oscillation in question is Raman active.

Effect of Crystal Orientation on the Raman Spectrum.—It has already been mentioned that when the Raman effect is studied with a single crystal, it is possible to obtain a wider range of information than that obtained when a crystal powder is used. For example, if we deal with a uniaxial crystal and designate the direction of the incident light by OX, that of the scattered light by OY and the vertical line by OZ, it is easily seen that three alternatives arise in respect of the nature of the incident light. It may be unpolarized or linearly polarized along OZ or linearly polarized along OY. In each one of these cases, the optic axis of the crystal may be placed parallel to either

OX or OY or OZ. Thus the number of alternative arrangements becomes nine. For each one of these settings, the scattered beam may either be photographed as such or only the horizontal component of it or only the vertical component of it may be photographed, thus enabling the observer to secure 27 separate spectra on the whole. The number will obviously be much larger for a biaxial crystal.

There has been some early work done by Schaefer, Matossi and Aderhold,[1] Miss Osborne,[2] Cabannes and Canals[3] and Michalke[4] on these lines. Amongst the more recent investigations, mention may be made of the work of Nedungadi[5] and of Bhagavantam[6] dealing with sodium nitrate and calcite respectively. The results obtained in these two cases are closely analogous to each other, as may be expected from the close similarity that exists between their structures. Some of their important conclusions will now be described. Fig. 26 is a diagram which gives an insight into the well-known structures of $CaCO_3$ and $NaNO_3$. The unit cell is a rhombohedron and contains two molecules. Only the non-equivalent atoms are shown in the figure. The plane equilateral CO_3 or the NO_3 configuration, as the case may be, is easily recognized in the figure. A number of them are piled up with their planes normal to the symmetry axis, which is also the optic axis of the crystal. There are only two lattice oscillations and three internal oscillations which are Raman active.[7] All the three internal oscillations are characterized by the fact that the movements of the individual atoms are confined to the symmetry plane only, whereas the two lattice oscillations are of a somewhat different type. This is reflected in the experimental results and it is connected with one of the most important observations of

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1 Z. f. Phys., *65*, 319 (1930).

2 Diss. Paris University (1932).

3 Comptes Rendus, *193*, 289 (1931).

4 Z. f. Phys., *108*, 748 (1938).

5 Proc. Ind. Acad. Sci., *10*, 197 (1939).

6 *Ibid.*, *11*, 62 (1940).

7 For a detailed analysis of the normal oscillations, reference may be made to Proc. Ind. Acad. Sci., *9*, 224 (1939).

Nedungadi and Bhagavantam relating to the reciprocal behaviour of the lattice oscillations on the one hand, and the internal

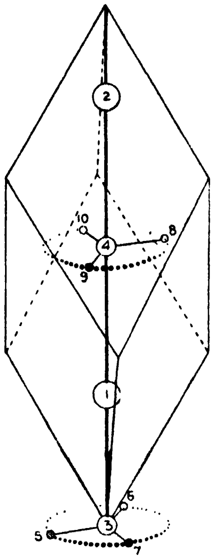


FIG. 26.

oscillations on the other. In the case of the internal oscillations, if the incident light vector is perpendicular to the plane of the triangle, the axis of the dipole giving rise to one of them, namely the total symmetric one, is also perpendicular to the same while the other two are not excited at all. On the other hand, if the incident light vector lies in the plane, the axes of the dipoles relating to all the three oscillations also lie in the plane. The strength of the dipole corresponding to the total symmetric oscillation is much more in the latter case than in the former. This results in the 1084 line of calcite and 1068 line of $NaNO_3$ being excited much more strongly when the incident light vector lies in the symmetry plane than when it is parallel to the optic axis. The behaviour of the lattice lines is fundamentally different. They usually disappear when the internal oscillations appear and *vice versa.* The polarization characters exhibited by these lines are also generally reciprocal of those exhibited by

the internal oscillations. From this, we have to conclude that so far as these oscillations are concerned, the axes of the corresponding dipoles are such that there are components both parallel and perpendicular to the incident light vector. It has been shown by Bhagavantam that all these results may be satisfactorily correlated with the symmetry properties of the crystal by considering the selection rules in detail.

In the foregoing paragraphs, only the bare outlines of the subject have been dealt with. The importance of studying the Raman effect in single crystals, in all its aspects, is just beginning to be realized. It may be confidently hoped that the subject of crystal physics will be considerably enriched by such investigations.

CHAPTER XV

EXPERIMENTAL TECHNIQUE

General.—Different experimental arrangements have been adopted by different investigators in order to suit the particular work under consideration. The details of the arrangement depend upon the nature of the substance under investigation. The three main items, ordinarily necessary for obtaining the Raman spectrum of a substance, are a suitable source giving a line spectrum for illuminating the substance, a container for the substance with transparent windows for illumination and observation and a spectrograph for the purpose of photographing the Raman spectrum. In cases where substances are available in the shape of large and transparent solid blocks such as gypsum, quartz or glass, the container may be dispensed with. There are many other auxiliary devices such as light filters, water circulation arrangement, reflectors, lenses, nicols and double image prisms, which are employed for special purposes. A general description of the arrangements will now be given and this will be followed by a detailed consideration of the improvements that have been effected in each direction.

Figs. *27a* and *27b* show two arrangements commonly employed for the study of the Raman spectrum of a liquid. In the first arrangement, originally adopted by Raman, the illumination is not strong. Wood suggested the second arrangement in which the proximity of the lamp to the Raman tube results in a large intensity of incident light. While the second arrangement possesses this valuable advantage, there are two points in favour of the first arrangement. These are: the direction of observation is nearly transverse though not strictly so and it is possible to eliminate effectively all stray light with a comparatively narrow tube. This method is therefore to be preferred whenever measurements of the intensity or polarization characters of the Raman lines are made, although it is relatively slow. The increased illumination in the second case carries with it the presence of rays in the incident light, which

exhibit a large deviation from transversality with respect to the direction in which the scattered beam is observed. It is

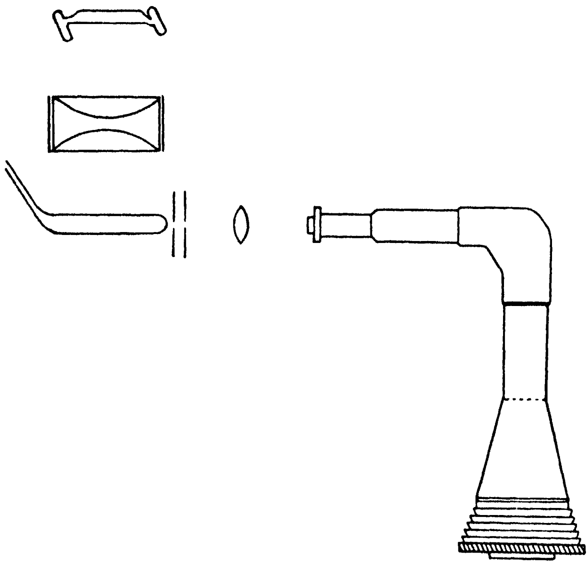


FIG. 27*a*.

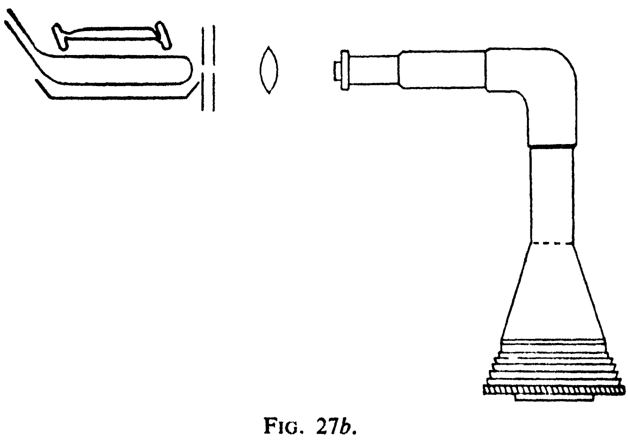


FIG. 27*b*.

also not so easy to effectively eliminate all parasitic light. As such, the latter method is somewhat unsuitable for the study of

the polarization and intensity characters but is eminently suited for obtaining rapidly the Raman spectra of substances. In the latter arrangement, it is usually necessary to prevent the Raman tube from being unduly heated by the lamp. This is achieved by circulating cold water in an outer jacket enveloping the tube. In this arrangement, reflectors of various shapes are also often located, either above or below the lamp or both, in order to further enhance the intensity of illumination. In both these arrangements, the rest of the apparatus is the same. A lens is used to focus the scattered beam on the slit of a spectrograph which is preferably of a high light gathering power.

Only slight modifications in the above arrangements are necessary for applying them to the case of gases. The liquid tube is simply replaced by a suitable container to hold the gas under investigation at a high pressure. The details of construction of such containers are dealt with a little later. In the case of solids, which are in the form of loose crystals or powders, certain essential modifications are necessary for successfully photographing the Raman spectra. These are mainly intended to avoid the masking effect due to a large amount of direct light coming out of the containers by repeated reflection at the crystal faces and entering the spectrograph. These will also be dealt with in the appropriate places.

Sources and Methods of Illumination.—An ideal source would be one which strongly emits a monochromatic radiation in the neighbourhood of 4000 A.U. In the absence of such a source, attempts are made to approach this ideal by using a suitable arc emitting a line spectrum in conjunction with a light filter. The sources now used may be broadly divided into two classes, namely, lamps employing mercury and lamps employing other substances. Under the category of mercury lamps, a variety of them have been constructed for different purposes. Besides the usual flat type mercury arc of about 6 inches length, which is the simplest and most commonly employed source, mention may be made here of the capillary lamps, spiral arcs, specially long arcs, the annular arc and so on. The shape of the arc depends to some extent on the nature of the investigation. Sometimes, more than one arc may be used with advantage.

Amongst the sources in which substances other than mercury are used as emitters, the helium lamp developed by Wood may be mentioned. This lamp, when surrounded by a filter of nickel oxide glass, furnishes a single wave-length (λ3888) for purposes of excitation and Wood [1] has employed this for obtaining several very nice Raman spectra. The whole spectrum is easy of interpretation because there is no overlapping by the Raman lines due to any other excitation as in the case of a mercury arc. As the manipulation and construction of this source is more difficult than the mercury arc, it has not been widely used in spite of its advantages. Krishnamurti [2] has used an arc consisting of a 50% tin-cadmium alloy for a study of the Raman spectra of coloured substances. Such lamps have also been constructed by Hoffman and Daniels.[3]

Some special methods of illumination have been used by certain investigators. Bär [4] has employed a long column of liquid and sent a parallel beam of light down the column and reflected it backwards. By examining the scattered light in the backward direction and slightly away from the incident light, considerable intensity may be obtained. This method of illumination is particularly useful for experiments with circularly polarized incident light.

Spectrographs.—An essential feature of a spectrograph, suitable for the study of Raman spectra, is high light gathering power. Good resolution combined with high light gathering power will make the instrument admirably suited for this work. Several instruments have been put on the market to answer these requirements. Daure [5] and Bourguel [6] have described spectrographs of great luminosity. An aperture ratio of at least F/7 is usually desirable in most cases. Cabannes and Rousset [7] have recently used a spectrograph having an aperture

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[1] Phil. Mag., *7*, 858 (1929).
[2] Ind. Jour. Phys., *5*, 587 (1930).
[3] Jour. Amer. Chem. Soc., *54*, 4226 (1932).
[4] Physikal. Z., *30*, 856 (1929).
[5] Rev. Optique, *7*, 45 (1928).
[6] *Ibid.*, *10*, 474 (1931).
[7] Comptes Rendus, *206*, 85 (1938).

ratio of F/0·7 for working with gases at normal pressures. Instruments of higher resolving power such as gratings have been used occasionally but are not to be recommended in view of their poor luminosity, which necessitates long exposures.

Billroth, Kohlrausch and Reitz[1] have developed a special type of spectrograph for a study of the Raman effect in crystal powders. Fig. 28 shows their arrangement. It consists of two

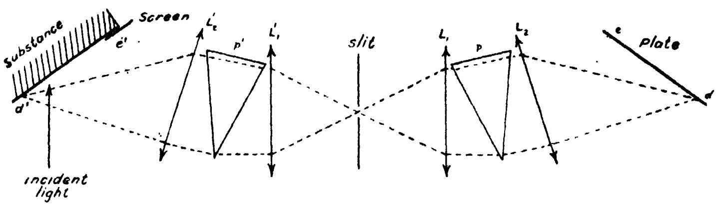


FIG. 28.

parts, each part having a prism and two lenses represented by the dashed and undashed letters respectively. The slit is common to both. The substance, which is in the form of a crystal powder, is illuminated with visible light in the usual manner. From the diagram, it may easily be seen that *e* and *e'*, and *d* and *d'* are conjugate positions. The image at *e* being that of λ4358 will mostly be formed by the light coming from *e'* and if *e'* is hidden with the help of a screen, the over-exposure of 4358 may be considerably prevented. This does not, however, affect the intensity of the Raman radiations as these are of altered wave-lengths and accordingly appear further up on the plate. The conjugate positions of such points are further down *e'* in the container and the slit is free to gather light from such positions. These authors have been able to work with very small quantities of substances by this method. The method is somewhat analogous, in principle, to the technique of complementary filters developed by Ananthakrishnan.

[1] Z. f. Elektrochemie, *43*, 292 (1937).

Containers.—The most suitable container for a liquid is a thin wall soda glass tube of about 1 inch internal diameter. One end is flattened and it constitutes the window through which the scattered light emerges out. The other end is drawn into the shape of a horn and blackened outside to provide a suitable background. This is slipped into a slightly wider tube which is provided with an inlet and an outlet. Either a suitable filter or cold water may be contained or circulated in the annular space as per the requirements of the work. The cooling jacket may be attached to the liquid tube with split rubbers and some cement. Such tubes are now made by various firms with transparent fused silica as the material. In such cases, a plane window is fused on the front and joints between the outer jacket and the inner tube are also effected by fusing. The sizes may, however, have to be altered to suit the quantities of liquids that are available for the investigation.

A special type of tube, shown in Fig. 29, has been developed by Pal and Sen Gupta[1] for a study of the Raman effect in liquids that are decomposed by exposure to light and hence need to be changed frequently. The liquid in the apparatus is continuously

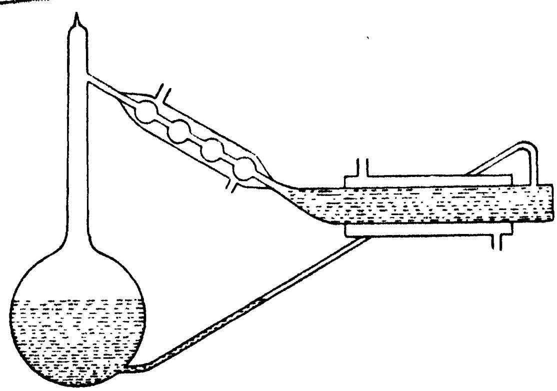


FIG. 29.

distilled and the decomposed matter is collected in the reservoir. Excellent Raman spectra may be obtained for liquids like

[1] Ind. Jour. Phys., 5, 609 (1930).

methyl iodide and aniline with such an apparatus. Tubes of other design, intended for continuous distillation have also been constructed by Murray and Andrews.[1]

Rasetti[2] was the first to develop a container for holding gases under high pressure. A description of his apparatus, which is shown diagrammatically in Fig. 30, is given below.

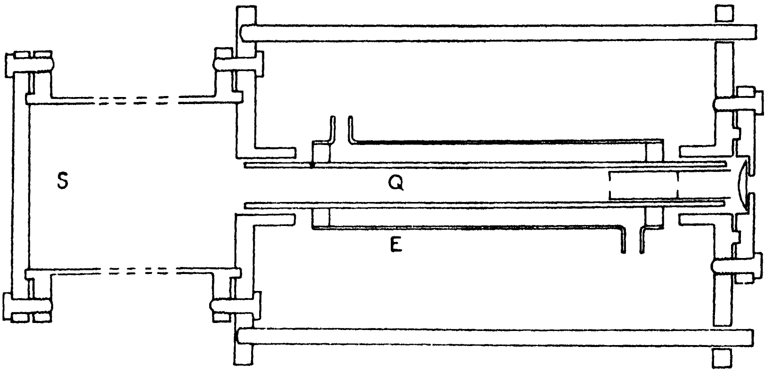


FIG. 30.

The apparatus is intended to withstand pressures of 10 to 15 atmospheres. Q is a thick wall quartz tube, having an internal diameter of 2·2 cms. and a length of 20 cms. This quartz tube is fastened to a large steel tube S by means of sealing wax. The external quartz tube E is filled with acetic acid in water in order to absorb the λ1849 radiation. This is done in order to prevent photo-chemical reactions in certain gases such as oxygen. λ2536 radiation of the mercury arc is used as the exciting radiation. The mercury arc is cooled by running water and the discharge is deflected towards the substance with the help of a strong magnet.

A container to stand pressures up to 50 atmospheres has been developed by Bhagavantam.[3] This apparatus is shown in Fig. 31. The gas is contained in a transparent silica tube having an inner diameter of $\frac{3}{4}''$ and an outer diameter of

[1] Jour. Chem. Phys., *1*, 406 (1933).
[2] Phys. Rev., *34*, 376 (1929).
[3] Ind. Jour. Phys., *6*, 319 (1931).

1¼″. This is enclosed in an outer steel tube T for protection. A circular glass window contained between thick rubber washers is pressed against the plane end of the quartz tube by a steel screw cap. The steel tube has a slit 6″×½″ cut out of it for illuminating the gas. The gas is admitted through a pin valve V attached to the screw cap C_2 at the back end of the quartz tube. An inclined black glass B is provided for securing a dark background. The outer surface of the silica tube is painted black leaving only a slit, in the same position and of the same size as the slit in the outer steel tube, for illumination of the gas. A system of painted apertures A is provided within the silica tube with the result that no light reflected by the walls of the tube enters the spectrograph. Pressures up to 50 atmospheres can be used in this apparatus and very good photographs are obtained in about 40 to 50 hours' time using λ3650, λ4046 and λ4358 as the exciting radiations.

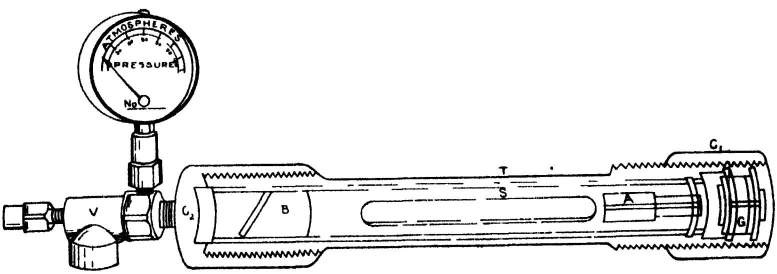


FIG 31

Houston and Lewis, Langseth, Trumpy and others have worked with gases under pressure, using slightly modified forms of apparatus. Wood employed a very long tube of HCl gas and obtained its Raman spectrum at atmospheric pressure using a specially made mercury arc.

Different types of containers for crystal powders have been developed from time to time. Menzies[1] and Bär[2]

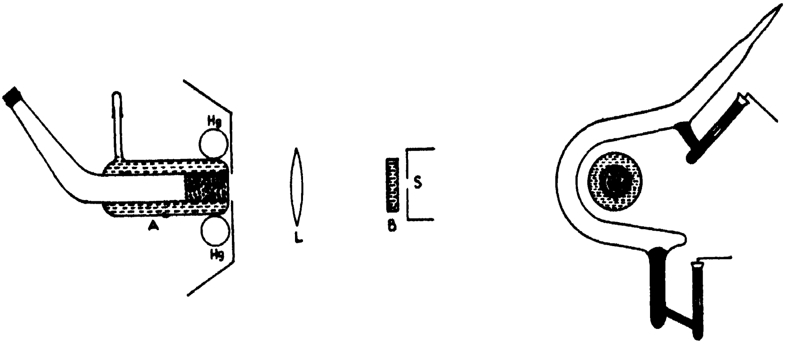
[1] Nature, *124*, 511 (1929). [2] *Ibid.*, 692 (1929).

were the first to obtain satisfactory Raman spectra from coarsely powdered crystals. The technique developed by these authors had opened up a wide field of research. Krishnamurti studied a large number of substances. The container used by him was a cell of triangular cross-section, two sides of the cell being silvered. The incident light entered through the third side. Ananthakrishnan[1] extended the work on crystals to a great variety of substances by using filters. The essential features of this method will be described in the next section.

The Use of Light Filters.—Filters have been used for four different purposes. As has already been mentioned, it is desirable to isolate a particular line, from the source such as the mercury arc, for purposes of excitation and to suppress all others. This is the primary use to which filters have been put. One of the two prominent mercury lines, namely, $\lambda 4046$ or $\lambda 4358$, is isolated and the other excluded in most investigations. An aqueous solution of sodium nitrite and a solution of iodine in CCl_4 may be mentioned as examples of filters which may be used to absorb 4046 and 4358 lines respectively. Filters have also been used to cut out the lines or the continuous spectrum in the source in certain regions so that Raman lines falling in these regions may be clearly recognized. The use of a concentrated solution of didymium chloride by Krishnamurti, in order to reduce the continuous spectrum in the source in the vicinity of $\lambda 4358$, may be mentioned as an example of this type of usage. A third use to which they have been put consists in just weakening one or the other of the two main lines $\lambda 4046$ and $\lambda 4358$ of the mercury arc. By studying each liquid with two filters successively, which weaken respectively the $\lambda 4046$ and $\lambda 4358$ lines, and by a visual comparison of the relative intensities of the lines on the two plates, proper assignment can be arrived at. Krishnamurti has made use of this method. Lastly, Ananthakrishnan has employed them for obtaining very good Raman spectra from crystal powders. His method consists in choosing a pair of filters which act in a complementary manner. One of them is interposed in the path of the incident light and

[1] See numerous papers in the Proc. Ind. Acad. Sci., *5* (1937).

the other in the path of the scattered light. His arrangement is shown in Fig. 32. In this figure, (*a*) shows the side view, and (*b*) is the section. The shape of the arc used is clear from (*b*).



(*a*) FIG. 32. (*b*)

Light from a mercury arc is first filtered through the filter A, consisting of a moderately strong solution of iodine in CCl_4, before being allowed to fall on the substance. This transmits λ4046 and all the other lines on the longer wave-length side are absorbed. The scattered light is then filtered through the filter B, consisting of a solution of $NaNO_2$, which freely transmits all the longer wave-lengths but considerably weakens λ4046. Such a procedure results in a vast improvement in the technique of the photography of the Raman spectra of crystal powders. Employing this method, Ananthakrishnan has obtained some very clear Raman spectra of crystal powders. Below is given a Table of some of the filters that have been used in Raman effect and the purposes for which they have been used.

TABLE LI

Description of Filters

Filter	Purpose	Remarks
Fairly saturated solution of $NaNO_2$	Absorbs λ4046, may be used in the technique of complementary filters	Widely used
Quinine sulphate solution	Absorbs λ4046 ..	Fluorescent, should be kept away from the Raman tube, not satisfactory
Potassium dichromate solution	Do. ..	Unsatisfactory
Iodine in CCl_4 (moderately strong)	Absorbs λ4358, may be used in the technique of complementary filters	Widely used
Iodine in CCl_4 (very dilute)	Absorbs λ4916 and λ5460, used for cleaning up this region	Widely used
Cobalt sulphocyanide solution	Absorbs λ4358	....
Dilute solution of sodium salt of O-cresolphthalein	Absorbs λ4046	....
Uranine solution ..	Absorbs λ4358	....
Didymium chloride solution	Weakens the continuous spectrum after λ4358 and isolates λ5460	....
M-dinotrobenzene in benzene	Do.	....
Nickel oxide glass ..	Transmits λ3889 of helium	Used by Wood
Acetic acid in water ..	Absorbs λ1849	Used by Rasetti
2% solution of *p*-nitrotoluene and one part in 50,000 of the rhodamine dye (5 GDN extra) in a 30 mm. thick layer	Absorbs all ultra-violet, transmits less than 1% of λ4047 and about 1% of λ4916 while transmitting more than 70% of λ4358	Used by Edsall and Wilson

Technique for Determining the Polarization of Raman Lines.— The simplest arrangement adopted for this purpose is shown diagrammatically in Fig. 33.

The light from a source S is condensed with the help of a condenser C into the substance contained in a Raman tube R.

The scattered light is focussed, with the help of a lens L, on the slit of the spectrograph. A suitably oriented double image

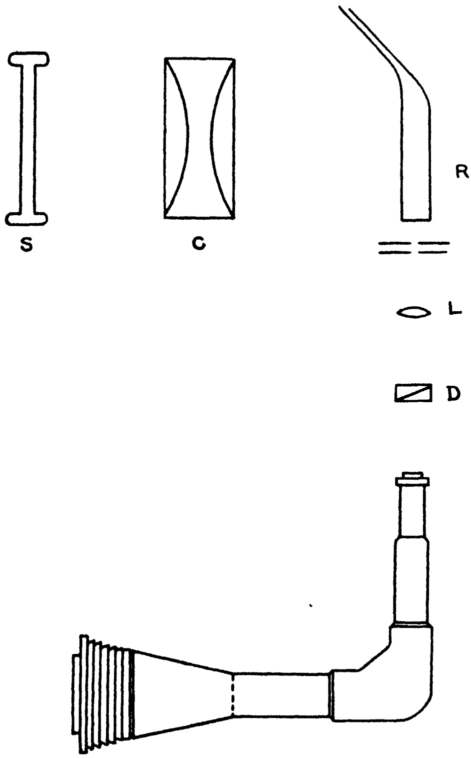


FIG. 33.

prism D separates the vertical and horizontal components in the scattered light and two images, one above the other, are accordingly formed on the slit. The two images are thus photographed simultaneously and any fluctuation in the intensity of the lamp will affect both to the same extent. It is not therefore necessary that the lamp should be maintained at constant intensity. The intensities of the two components for any given line are then compared by one of the usual methods employed for comparison of intensities of two beams of the same wavelength. For instance, a set of intensity marks from a constant

intensity source may be given on the same plate by the method of varying slit widths[1] and a density-log intensity curve drawn for the wave-length in question. With the help of the curve, the ratio of the intensities of the two components is obtained.

The above description is greatly simplified and there are many precautions that one has to take in practice, before one can get reasonably accurate values of the depolarization factors. Great many additions and modifications have been made to the arrangement shown in Fig. 33 by various investigators with a view to eliminate or minimize these errors. These will now be briefly enumerated.

(*a*) *Crystalline quartz to be avoided.*—Quartz condensers, quartz spectrographs and quartz windows should not be used in the arrangement unless it be that they are made of fused quartz. The optical activity of crystalline quartz introduces great complications into the experiments on polarization.

(*b*) *Strain-free windows.*—The window of R through which the scattered light is viewed should be strain-free. Otherwise, birefringence due to its photoelastic properties sets in and vitiates the results. This is particularly important when work is being carried on with gases under pressure or when windows are fused on to tubes. Plane windows are to be preferred to those having a curvature.

(*c*) *Polarization due to oblique refraction at the prism surfaces.*—In accordance with the well-known Fresnel's laws of reflection and refraction, the horizontal and the vertical components are, in general, neither reflected nor transmitted equally by transparent media. As a result, the depolarization of any radiation, passing obliquely through the prisms of the spectrograph, is altered: the vertical component loses more than the horizontal one in the usual arrangement and the depolarization is apparently enhanced. The error introduced in this manner is, however, a constant, characteristic of the instrument used. It may be determined very exactly by allowing unpolarized light to fall on the slit of the spectrograph and determining its state of polarization as it emerges out at the other end.

[1] The details of this method are given in the next section.

There are also other methods of eliminating this error. A birefringent substance like a mica plate may be introduced in front of the slit so as to compensate for the unequal loss. Alternatively, a Nicol prism whose vibration axis is at 45° to the vertical or horizontal may similarly be introduced. In this case, only $H \cos^2 45$ and $V \cos^2 45$ and not the full intensities H and V are allowed to fall on the slit. It is easily seen that the ratio and hence ρ remains unaltered, whereas the direction of vibration in both images is brought to 45° with the vertical or the horizontal. Under such circumstances, both the images suffer the same loss on being transmitted through the instrument. Yet another alternative is available and a specially constructed double image prism, so made that when the separation of the two rays is in the vertical position, the vibrations in the components are inclined to the vertical at 45° may be used for this purpose. The error is automatically eliminated in this case but the incident light should be arranged to fall on the tube at a suitable angle and the usual arrangement altered accordingly.

(*d*) *Lack of transversality in the incident beam.*—It has already been pointed out in the earlier chapters that, when unpolarized incident light is used, the depolarization of the scattered light is a minimum in the transverse direction and goes on increasing on its either side with increasing obliquity till it becomes completely unpolarized in directions which are parallel to that of the propagation of the incident beam. Thus, it appears necessary that, in order to obtain experimentally the true depolarization in the transverse direction, one has to use a strictly parallel incident beam and make the observation at an angle of 90° with it. This arrangement is, however, impracticable in the case of Raman scattering and the alternative arrangement shown in Fig. 33 involves a lack of transversality for which a correction has to be made. This correction is somewhat of a varying magnitude, being largest for well-polarized lines and smallest for depolarized lines. An estimate of this is best made by taking a few standard liquids for which the depolarization values are obtained in respect of Rayleigh scattering with ideal arrangements and re-investigating them with the arrangements shown in Fig. 33. A curve showing the magnitude of this error

and its dependence on the initial depolarization may be drawn and utilized for applying the correction in an unknown case. The correction on this score usually ranges about 8% with a 8-inch condenser and 6-inch mercury lamp and has to be subtracted from the values obtained. Attempts have also been made to avoid this correction by adopting a different method of illumination in which the condenser is replaced by a system of linear slits, thus avoiding angles but such an arrangement results in a very low efficiency.

(*e*) *Effect of slit width.*—The width of the slit has a two-fold effect on the results. Excessively narrow slits introduce a polarization of their own in the light that gets through them and should therefore be avoided. The width of the slit also affects the width of the line under investigation. Since a partially polarized Raman line is always accompanied by rotational scattering as well, a broadened-out line will include in itself, part of the latter type of scattering which is depolarized to the limit. The result obtained will be some intermediate value and is thus easily seen to depend on the slit width. This error becomes particularly important when we are working with liquids, where the wings are not usually well separated from the Q branches and it is absolutely necessary to specify the width of the slit at which the work has been carried out. One has also to guard against the possibility of partially overlapping components of different states of polarization, giving mean values when wide slits are used.

Edsall and Wilson [1] have described a simple and rapid method of qualitatively ascertaining the state of polarization of Raman lines using a Polaroid. The illumination in their arrangements is obtained from four vertical mercury lamps, equipped with parabolic reflectors which sorround the Raman tube. Between the Raman tube and the lamps is slipped a cylindrical Polaroid, so made that it transmits only light polarized with its electric vector parallel to the axis of the cylinder. Two exposures are made, using alternatively full intensity with the

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[1] Jour. Chem. Phys., *6*, 124 (1938).

Polaroid in position and diminished intensity with the Polaroid removed. Such a diminution in the incident intensity in the latter case is brought about in order to compensate for the absorption by the Polaroid. It is so arranged that the times of exposure in the two cases are more or less the same. Under these conditions, it is easily shown that the polarized Raman lines will decrease in intensity much more than the depolarized ones. If the relative intensities of illumination are so arranged that the depolarized Raman lines are of equal intensity in the two cases, the polarized ones will stand out very prominently by their feebler appearance in the exposure without the Polaroid. In this way, they have obtained results which are in satisfactory agreement with those obtained by employing the usual methods. These authors have also used a plane Polaroid disc as an ordinary polarizer in the incident beam and obtained similar results by taking two pictures by placing the axis of the Polaroid alternately vertical and horizontal.

Technique for Determining the Intensities of Raman Lines.—Owing to the extreme feebleness of Raman lines, the problem of experimentally determining their intensities is beset with numerous difficulties. The main issues that arise under this section are dealt with serially below.

The first problem relates to the determination of the absolute intensities of Raman lines, i.e., in relation to the exciting line. No accurate data are available with regard to the absolute intensities of Raman lines either in liquids or gases. In respect of liquids, there are wide divergences between the results of various authors, as may be seen from Tables XXVI, XXVII and XXVIII. In respect of gases, only estimates have been made by Bhagavantam. On account of the great disparity between the intensities of the Raman and the Rayleigh lines, a direct comparison is not possible by the rigorous methods of intensity measurements. Some intermediate standard has to be adopted to obtain reasonably accurate values and several alternative possibilities may be suggested for this purpose. The weaker Rayleigh lines such as the satellites of $\lambda 4358$ or $\lambda 4077$ and $\lambda 4108$ accompanying $\lambda 4046$ will serve as intermediate

standards, according as the former or the latter is used as the exciting radiation. The introduction of a narrow neutral strip, having a known absorption coefficient, just in front of the photographic plate in the region where the parent line is recorded may be more satisfactory. In the case of liquids, these determinations are somewhat difficult of interpretation in view of the intense unresolved continuous spectrum that is usually present alongside the Rayleigh as well as vibrational Raman lines.

The second problem relates to the determination of relative intensities of a set of Raman lines excited on the Stokes side by a given parent line. This is not so difficult as the above, although great care has to be taken even here in comparing the intensities of lines having different depolarization factors and different structural properties. On account of the neglect of the latter factors, very divergent results have been reported in the literature in the past.

The third relates to the determination of the relative intensities of Stokes and anti-Stokes Raman lines. In view of the importance of an experimental determination of this ratio, some care has been bestowed by Ornstein, Rekveld and Sirkar on this problem. The results of Sirkar have already been quoted. By restricting ourselves to substances in which the Raman shifts are not large, we can choose pairs of lines whose intensities are not very different and an accurate comparison can be effected with the usual methods.

The fourth relates to the determination of the distribution of intensity either amongst the fine structure components of a vibrational line or within the line itself when it has a breadth. There are no serious experimental difficulties in the way of this work, provided the fine structure components are all more or less similarly polarized and an instrument of sufficiently high dispersion, so as to eliminate overlapping, is used.

Lastly, there is the question of verifying the Rayleigh fourth power law amongst the Raman lines which is the same thing as determining the influence of the exciting frequency on their intensities. As the characteristic frequency of the molecule is approached, we should expect a pronounced deviation from

the fourth power law and such deviations have been measured by a number of workers.[1]

The general method of measuring intensities is as follows. For a detailed consideration of the various errors involved and their discussion, reference must be made to standard works relating to photographic photometry. Only a brief description will be given here. Photographic plates which have a reasonably large and more or less uniform sensitivity in the region of investigation should be used. The densities obtained for the lines under comparison should be measured with some form of a microphotometer. On each plate, a set of calibration spectra should be recorded with the help of a step-filter or by the method of varying slit widths. The continuous radiation used for this purpose should be obtained from an emitter having a known energy distribution. In the method of varying slit widths, it is further necessary that the emitter should be fed by a steady current and be made to keep constant intensity. With the help of these calibration marks, it is possible to draw density curves for each wave-length. The intensities corresponding to any density are obtained from these curves. Inter-comparison of different wave-lengths is easily made because the distribution of energy in the source amongst the different wave-lengths is known. The exposure times necessary to obtain the Raman spectra and the calibration spectra should not differ very widely. Corrections should be made for any continuous background that might appear on the plate.

Besides the above points which are common to all intensity measurements, some special features characteristic of the measurements in Raman effect may now be mentioned. The measured intensities of Raman lines should be corrected for the absorption in the body of the liquid contained in the Raman tube. The oblique refraction at the prism surfaces in a spectrograph affects the aggregate intensities of differently polarized lines to different extents. A correction has to be applied on this

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[1] Rekveld, Dissertation to the University of Utrecht (1931).
Sirkar, Ind. Jour. Phys., *5*, 159, 593 and 663 (1930).
M. Werth, Phys. Rev., *36*, 1096 (1930) and *39*, 299 (1932).

score. This correction is different for different methods of illumination. It ceases to be of importance when we are comparing lines possessing the same depolarization factor.[1] The structure of the line and the slit width employed affect the results with regard to relative intensities. It is best to compare the peak intensities of lines having the same structure and the aggregate intensities of lines having different structures. These issues give rise to several errors, particularly in the case of Raman lines in liquids where they possess widely varying characters of breadth, fine structure and polarization.

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[1] Veerabhadra Rao, Proc. Ind. Acad. Sci., *7*, 208 (1938).

CHAPTER XVI

RAMAN EFFECT IN RELATION TO INORGANIC CHEMISTRY

Nature of Valency.—Krishnamurti studied the Raman effect in a large number of halides and classified them into three groups as follows :—

1. Those that show strong Raman lines, such as the chlorides of Hg(ous), Hg(ic), P, As, Sb, C, Si, Ti, Sn and hydrogen.
2. Those that show faint Raman lines, such as $BiCl_3$, $ZnCl_2$, CdI_2 and $AuCl_3$.
3. Those that show no lines at all, such as the chlorides of Na,[1] K, NH_4, Ba, Ag, Cu(ic), Cd, Mg, Sn(ous), Th, as well as $CdBr_2$, PbI_2, KI, LiF, NaF, CaF_2.

It is obvious from this classification that the chlorides of the strongly electropositive elements do not show the Raman lines while the chlorides of the non-metals and metalloids show it very well. It is also known that the former type of compounds have a large electrical conductivity in the fused state whereas the latter have a comparatively low conductivity. These and other features enable us to distinguish between the two major types of chemical linkages, namely, covalent and electrovalent. Wherever the linking is of a covalent type, the Raman lines appear with great intensity and the reverse is the case when linkages of an electrovalent type occur. The fact that the entire body of organic compounds, mostly characterized by covalent linkages, exhibit prominent Raman spectra may be taken as further evidence in support of the above conclusions.

Such a close dependence of the intensity of the Raman lines on the chemical nature of the linkage is not very surprising, if we recall what has been said in the earlier chapters dealing with the theory of the Raman effect. The intensity of a Raman

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[1] Sodium chloride exhibits a very weak band due to second order terms.

line is determined essentially by two factors, namely, the symmetry of the molecule and the extent to which its polarizability is affected by the oscillation in question. If the polarizability of a molecule is either totally independent of or very insensitive to variations in the nuclear distances, as is likely to be the case when the electrons have definitely gone over from one nucleus to the other in molecule formation (electrovalent), nuclear oscillations will cause little or no alteration in the polarizability and will not consequently give rise to Raman lines. On the other hand, if the binding electrons remain common to the nuclei (covalent), the polarizability of the molecule will naturally be considerably affected by the positions of the nuclei and the nuclear oscillations will be accompanied by appreciable variations of the polarizability. They will consequently give rise to Raman lines.

The force constants, calculated with the help of the Raman frequencies, for different types of carbon-carbon linkages are given below.

Link	Substance	$F \times 10^{-5}$
$C \equiv C$	C_2H_2	14·0
$C = C$	C_2H_4	10·8
$C — C$	C_2H_6	4·4

It is very significant that the values in the three cases are quite distinct and are roughly in the ratio of 3 : 2 : 1. This result, coupled with the fact already noted under diatomic molecules that the F values usually fall into three regions, suggests that the chemical classification of the bonds into triple, double and single ones is reflected here. The binding strength of a triple bond is about thrice and that of a double bond is about twice that of a single bond. This does not, however, imply that the chemical stability of these bonds is in this order. It is, in fact, known to be in the reverse order.

Complex Compounds.—From what has been said in the foregoing, it is obvious that the Raman spectrum is characteristic of the molecular structure. Marked changes may therefore be expected to take place when a complex, consisting of one or more like or unlike molecules, is formed. Different names

such as polymerization, co-ordination, dipole association, etc., have been given to such phenomena and these are intended to convey that the mechanism of the complex formation may be different in different cases. The formation of a distinctly different chemical structure as in $S_2O_6 \rightleftarrows 2SO_3$ or in $N_2O_4 \rightleftarrows 2NO_2$, etc., may be regarded as coming under the class of polymerization. The Raman spectrum of sulphur trioxide at the room temperature has been found to exhibit, besides others, nine prominent Raman frequencies, namely 290, 370, 534, 666, 697, 1068, 1271, 1403 and 1489. On heating to about 100°C., three of these frequencies, namely 534, 1068 and 1403 are found to get relatively brighter and these are attributed to SO_3. The phenomenon is perfectly reversible and may be utilized for making a quantitative study of the relative proportions of the two structures. The case of $N_2O_4 \rightleftarrows 2NO_2$ is, however, not so straightforward as NO_2 is a highly coloured substance. The interesting series of polymers of methyl esters of silicic acid have been studied by Weiler. The association of the hydroxyl group of one molecule with the hydroxyl group of another through a co-ordinate link, as per the scheme given below, may be regarded as a typical example of co-ordination.

$$\mathrm{R{-}O{-}H} \leftarrow \underset{}{\overset{\mathrm{R}\atop|}{\mathrm{O}}}\mathrm{{-}H}.$$

The case of water, in which some of the Raman bands have been attributed to $(H_2O)_2$ and $(H_2O)_3$ molecules, is probably an example of this type of complex formation. Many other complexes which are known to be of a co-ordination type and others which are of a doubtful nature have been investigated. Amongst those studied are copper, zinc and cadmium ammonium complexes, some complex cyanides, K_2HgCl_4, $KCdCl_3$, molybdates, tungstates, etc. Dipole association is only a type of loose adherence of dipole molecules and usually does not result in the appearance of new Raman lines. The existing Raman lines are, however, shifted or broadened very considerably. The considerable breadth of the Raman lines in liquid ammonia and water may be attributed, at least in part, to this type of association.

Mixed Molecules and Mixed Crystals.—As has already been pointed out, the Raman spectrum method is very well suited for a study of the formation of new complexes as this is usually accompanied by the appearance of new lines. A study of the intensities of these new lines and the determination of the concentration at which the intensities are a maximum will throw light on the constitution of the mixed molecules. Several very interesting cases of mixed molecule formation have been studied by Trumpy,[1] Burkard[2] and others. In mixtures of $SnCl_4$ and $SnBr_4$, Trumpy observed new lines at different concentrations which may be ascribed respectively to $SnCl_3Br$, $SnCl_2Br_2$ and $SnClBr_3$. Similarly, with mixtures containing two parts of PCl_3 and one part of PBr_3, and two parts of PBr_3 and one part of PCl_3, he detected the presence of PCl_2Br and $PClBr_2$ respectively. Burkard made a more extensive study of these mixtures and the intensity variations of their Raman lines. He found that the strongest line that can be attributed to the mixed molecule $PClBr_2$ is at about 240 and has a maximum intensity in the mixture $3PCl_3+6PBr_3$ as may be expected. He also noticed marked shifts in the lines of the pure molecules themselves.

Mixed crystals of *p*-dichlorobenzene and *p*-dibromobenzene of varying compositions have been studied by Vuks[3] and Sirkar and Bishui.[4] The results obtained by these authors are not in agreement with one another and hence a detailed discussion will not be attempted here. Vuks observed a progressive alteration of the frequencies from one set to the other as the composition changes whereas the latter authors contradicted this statement.

Isotopes.—The substitution of an isotopic atom instead of the original one in a molecule alters both the symmetry of the molecule and the effective mass. The former affects the selection rules, degeneracy and polarization factors whereas the latter alters the magnitudes of the characteristic frequencies. Both

[1] Z. f. Phys., *66*, 790 (1930) and *68*, 675 (1931).
[2] Z. f. Phys. Chem. (B), *30*, 298 (1935).
[3] Acta. Phys. Chem. U.R.S.S., *6*, 327 (1937).
[4] Ind. Jour. Phys., *11*, 417 (1938).

these consequences are manifested in the Raman spectrum and offer a wide field for investigation. Amongst the isotopes that have so far been studied from this point of view are those of hydrogen, carbon and chlorine. A few typical cases will be dealt with here. The Raman spectra of the isotopic molecules H_2, HD and D_2 have been investigated very completely. The phenomenon of alternating intensities in the rotational Raman spectra is observed in the symmetrical molecules of H_2 and D_2 but is altogether absent in HD as may be expected. The substitution of D for one of the hydrogens destroys the symmetry. Their vibrational frequencies 4156, 3631 and 2992 are respectively in the ratio of $\sqrt{2} : \sqrt{\frac{3}{2}} : 1$. Some of the compounds, obtained by substituting deuterium for hydrogen in benzene, have been studied. These results are of particular help in interpreting the spectrum of benzene in relation to its constitution. The seven Raman active normal frequencies of C_6H_6 and C_6D_6 are shown below.

C_6H_6 :	606	849	992	1178	1585—1606	3047	3062
C_6D_6 :	581	669	945	873	1548	2266	2293

Quite a large number of other organic compounds in which deuterium has taken the place of hydrogen have also yielded very valuable results.

The Raman spectrum of CCl_4 has been studied by Langseth[1] and others in great detail from the point of view of chlorine isotopes. The five different molecules that are possible, their relative abundances and their symmetries are given in Table LII,

TABLE LII

Isotopic Constitution of CCl_4 Molecule

Molecule	Point group	Number of Raman lines expected	% abundance
CCl_4^{35} ..	T_d	4	33·5
CCl_3^{35} Cl^{37} ..	C_{3v}	6	42·2
CCl_2^{35} Cl_2^{37} ..	C_{2v}	9	19·8
CCl^{35} Cl_3^{37} ..	C_{3v}	6	4·2
CCl_4^{37} ..	T_d	4	0·3

[1] Z. f. Phys., *72*, 350 (1931).

on the assumption that Cl^{35} and Cl^{37} occur in the ratio of 3·185 : 1.

The last two varieties are in such small proportions that we may not expect to record, ordinarily, the Raman lines due to them. The spectrum obtained with CCl_4 should therefore be a superposition of the results to be expected of the first three varieties. Table LIII contains the results of calculations recently carried out by Wu and Sutherland[1] along with the observations of Langseth. The letters given under CCl_4^{35} have the same significance as in the character Table for tetrahedral molecules. Numbers in brackets represent degeneracies.

TABLE LIII

Isotopic Components in the Raman Spectrum of CCl_4

CCl_4^{35}	$CCl_3^{35}Cl^{37}$	$CCl_2^{35}\ Cl_2^{37}$	Calculated cm.$^{-1}$	Observed cm.$^{-1}$
$(A_1)\nu_1$ (1)	ν_1' (1)	ν_1'' (1)	$\nu_1-\nu'_1=\nu'_1-\nu''_1=3{\cdot}15$	$\nu_1-\nu_1'=3{\cdot}10$; $\nu_1'-\nu_1''=3{\cdot}20$
$(E)\nu_2$ (2)	ν_2' (2)	ν''_{2a} (1)	$\nu_2-\nu''_{2a}=\nu_2-\nu''_{2b}=2{\cdot}91$	Doublet with a spacing of 2·2
		ν''_{2b} (1)	$\nu_2-\nu_2'=1{\cdot}46$	
$(F_2)\nu_3$ (3)	ν'_{3ab} (2)	ν''_{3a} (1)	Complicated by the fact of its being a doublet	Unresolved
	ν'_{3c} (1)	ν''_{3b} (1)		
		ν''_3 (1)		
$(F_2)\nu_4$ (3)	ν'_{4ab} (2)	ν''_{4a} (1)	Six components at distances 1·5, 0·5, 0·9, 1·3 and 1·2	Doublet with a spacing of 2·93
	ν'_{4c} (1)	ν''_{4b} (1)		
		ν''_{4c} (1)		

Although the observed results are not apparently in entire agreement with the theory, Wu and Sutherland have shown, from a detailed consideration of both, that better agreement could not have been obtained under the conditions that prevailed in Langseth's work. An investigation under much higher dispersion than has been used by Langseth is obviously desirable. In a similar manner, a variety of other compounds may be studied and very valuable information obtained particularly

[1] Jour. Chem. Phys., *6*, 114 (1938).

regarding the fine structure of vibrational lines where it is due to the isotopic constitution of the molecule. A study of the carbon isotope has been pursued in benzene and several other organic compounds. The principal line at 992 in benzene due to a symmetric expansion of the hexagonal ring has a companion at 984 which may now be definitely attributed to the $C_5^{12}\,C^{13}\,H_6$ molecule.

Water of Crystallization.—Nisi[1] and Ananthakrishnan[2] have made a systematic study of the Raman spectra of several crystals containing water of crystallization. Their results are summarized in Table LIV.

TABLE LIV

Raman Bands due to Water of Crystallization

Crystal	Frequencies	Remarks
$LiSO_4 . H_2O$ ..	3438	....
$Na_2SO_4 . 10H_2O$ ..	3438	....
$Al.K(SO_4)_2 . 12H_2O$	3384	....
$MgSO_4 . 10H_2O$ ..	3227 3445	....
$CdSO_4 . \frac{8}{3} H_2O$ ..	3423	....
$CaSO_4 . 2H_2O$ ..	3404 3497	Fairly sharp
$CuSO_4 . 5H_2O$ ..	3221 3377 3494	Nisi
,, ..	3172 (3*bd*) 3367 (2*bd*) 3470 (1*bd*)	Ananthakrishnan
$Na_2S_2O_3 . 5H_2O$.	3337(?) 3414	....
$C_4H_4O_6K . Na . 4H_2O$	3303 3405	....
$Mg(NO_3)_2 . 6H_2O$ ..	3250(1*b*) 3370 (4*bd*) 3495(3*bd*) 3590(5*b*)	Central two merge into each other
$Ca(NO_3)_2 . 4H_2O$ ..	3256 (1*b*) 3500 (3*bd*) 3600 (2*b*)	Broad and merging into each other
$Cd(NO_3)_2 . 4H_2O$ ..	Similar to above	Do.
$Cu(NO_3)_2 . 3H_2O$ ..	3150 (½) 3338 (2) 3503 (2) 3570 (1)	Fairly sharp lines
$Ce(NO_3)_3 . 6H_2O$ ..	3257 3400 3152	Last two are not well resolved
$Bi (NO_3)_3 . 5H_2O$ ..	3170–3430 3467 (2*b*) 3557 (3*b*)	First is a very broad band
$SrCl_2 . 6H_2O$ ..	3217 (1) 3284 (½) 3363 (2) 3433 (10*b*)	Last one is very intense
$MgCl_2 . 6H_2O$ ..	1600 (0*b*) 3173 (1*b*) 3338 (10*b*) 3395 (6*b*) 3512 (10*b*)	....
$MnCl_2 . 4H_2O$ ..	3312 (2*b*) 3395 (2*b*)	An additional diffuse band besides these two
$Na_3VO_4 . 12H_2O$ ..	3150–3467 3636	....
$Na_3PO_4 . 12H_2O$ ..	Similar to above	....
$Na_2CO_3 . 10H_2O$ ..	3150–3600	One broad band
$Na_2B_4O_7 . 10H_2O$ ..	3172 (2) 3312 (2) 3432 (4*b*) 3500 (½) 3535 (½) 3580 (4*c*)	Fairly sharp lines

[1] Jap. Jour. Phys., *7*, 1 (1931).

[2] Proc. Ind. Acad. Sci., *5*, 446 (1937).

The following results of these authors in respect of bands due to water of crystallization may be noted. The character and the number of the bands vary very considerably from substance to substance, as may be seen from the Table. In certain cases like $Na_2B_4O_7 . 10H_2O$ and $Cu(NO_3)_2 . 3H_2O$, the bands are fairly sharp and well separated. In certain other cases, the entire Raman radiation consists of very broad bands which can hardly be resolved from each other. The intensities also vary from substance to substance, the chlorides of calcium, strontium and magnesium showing particularly intense bands.

The relative intensities of the bands given by gypsum show striking variations with varying directions of observation and illumination. Some results in this direction have been obtained by Schaefer, Matossi and Aderhold[1]. A satisfactory interpretation of such amazing variations is at present very difficult and the subject offers much scope for further work.

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[1] Z. f. Phys., *65*, 319 (1930).

CHAPTER XVII

RAMAN EFFECT IN RELATION TO PHYSICAL CHEMISTRY

Nature of the Liquid State.—Certain aspects of Raman effect have thrown considerable light on important problems in physical chemistry. As the foremost amongst these, we shall now consider the nature of the liquid state. We have already treated in detail, the consequences of the molecule exchanging rotational or vibrational energy with the light quantum but the case of translational energy has only been briefly mentioned in connection with the fine structure of Rayleigh lines. If we are dealing with gaseous molecules, it is quite easy to see that the Rayleigh scattering, which has to be regarded as being emitted by moving instead of stationary centres, will be spread out in accordance with the simple Maxwellian distribution of velocities. The broadening will depend on the direction of observation, being zero in the direction of the incident rays and maximum in the opposite direction. The other extreme is that of a solid and this

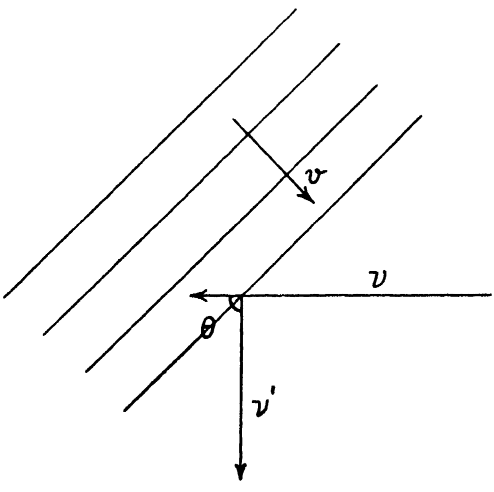


FIG. 34.

was first dealt with by Brillouin on the basis of the Einstein theory of scattering by dense media. If we disregard the molecular structure and replace the solid by a homogeneous elastic continuum, the translatory motions may all be resolved into a system of sound waves traversing the solid in all directions. There will be selective reflection as shown in Fig. 34. The velocity v of the sound wave may be resolved into $v \sin \frac{\theta}{2}$ along the direction of observation and $v \cos \frac{\theta}{2}$ in a direction perpendicular thereto. The former causes a doppler shift such that

$$\frac{\nu}{\nu'} = \frac{c - v \sin \frac{\theta}{2}}{c + v \sin \frac{\theta}{2}},$$

$$\text{or} \quad \nu' - \nu = 2\frac{\nu}{c} \cdot v \sin \frac{\theta}{2}.$$

If we have a wave receding backwards also we get

$$d\nu = \pm 2\frac{\nu}{c} \cdot v \sin \frac{\theta}{2}. \quad \ldots \quad \ldots \quad (1)$$

Equation (1) tells us that the scattered light should merely consist of two displaced components, the displacement depending upon the velocity of sound in the medium and the angle of scattering. It has not been hitherto possible to put these simple theories to an extensive test in either the gases or solids[1] but a very vast amount of experimental work has been done with liquids. Gross was the first to publish a series of results on the fine structure of the Rayleigh line. He was followed by several investigators who used different high resolving power instruments and the subject received considerable attention in recent years. Using specially made mercury arcs and a Fabry-Perot Etalon, Raman and Raghavendra Rao have tackled the problem systematically and their results will be briefly noted here.

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[1] The results to be expected in the case of crystals are more complicated. There are three different sound velocities associated with a given direction in a crystal and we should accordingly expect six Brillouin components in general. Raman and Venkateswaran [Nature, *142*, 250 (1938)] have recently succeeded in recording and reproducing these components in gypsum.

The Brillouin components have been recorded in a large number of liquids. The dependence of the shifts, on the angle of scattering and on the frequency of the incident radiation, has been found to be in complete accordance with that predicted by the Brillouin formula (1). Besides the Brillouin components, a central component which is distinctly brighter than the two displaced components has been recorded in all the liquids studied. In certain liquids such as CCl_4, the central component is relatively much brighter than the outer ones whereas in liquids like toluene, the disparity is not so striking although the central one is still the brighter of the three. The effect of increasing the temperature is to make the Brillouin components fainter and broader while the central component gets brighter. The Brillouin components tend to merge into the centre. A diminution of the temperature has the reverse effect. The two Brillouin components are found to be completely polarized in transverse scattering. The central component is also practically completely polarized in non-polar liquids. In liquids composed of highly optically anisotropic molecules, there is a strong continuous background in the region of these components. In strongly associating liquids like formic and acetic acids, the central component shows an appreciable depolarization. In viscous liquids, the Brillouin components are somewhat faint. On heating, the viscosity becomes less and the components gather strength.

The interpretation of these results, in the light of the Brillouin theory, is closely connected with the nature of the liquid state. The presence of the outer components lends support to the idea that the translational energy may be replaced by a system of sound waves not only in a solid but also in a liquid. The presence of the central component also, in liquids, gives further information as it is not to be expected in a case where all the thermal energy (excluding that due to internal degrees of freedom) is in the form of sound waves. It should be explained by postulating that a portion of the movements are of the random type as in a gas. That the central component is always brighter may be connected with the well-known result that gaseous Rayleigh scattering is always much brighter, molecule per

molecule, than the corresponding scattering from either liquids or solids. The variations in the relative intensities of the central and the outer components from liquid to liquid may be taken to furnish a rough idea as to how the thermal energy is apportioned between the two types in each liquid. That the Brillouin components get fainter and broader and gradually merge into the centre with increasing temperature is also to be expected on the above picture. The complete polarization of the central as well as the Brillouin components indicates that they consist entirely of the isotropic scattering. The question as to where the anisotropic scattering is located then naturally arises. There appears to be no definite answer available to this question from the existing data.

The prominent continuous background observed in this region with highly anisotropic molecules is undoubtedly to be identified with the anisotropic scattering but such an identification leads to the surprising result that the anisotropic scattering is present even in regions which are so close as a fraction of a wave number to the centre. The appreciable depolarization of the central component observed in strongly associating liquids suggests the presence of large groups which are practically unable to rotate in such liquids. The feebleness of Brillouin components in viscous liquids is presumably due to the fact that the sound waves, though present, are quickly damped out and do not extend over ranges sufficiently long as to cause regular reflection. The effect of increasing temperature and diminishing viscosity on this result is obvious. We thus get an intimate picture of the relationship of the liquid state to the gaseous state on the one hand and the solid state on the other. An important feature, namely, the presence of both types of thermal energy—one in which it is organized in the manner of sound waves and the other in which it is akin to a random type—ordinarily characterizes the liquid state. Complications such as viscosity may affect the extent of these sound waves and the consequences have to be taken into account before interpreting the results. All the above work is mostly of a qualitative nature. Quantitative measurements of intensity of the various com-

ponents under different physical conditions promises to be of great value.

Landau and Placzek[1] have recently concluded that the ratio of the intensity of the two displaced components together to that of the aggregate Rayleigh scattering should be C_p/C_v. It follows from this that the intensities of the three components should be in the proportion $\frac{C_v}{2} : C_p - C_v : \frac{C_v}{2}$. Birus[2] has made a preliminary study of this problem and obtained results, in a few cases, which show a fair agreement with the above conclusion. It is interesting to note that in the case of water for which C_p and C_v are very nearly equal, the central component is barely detectable. This relation is easily derived in the following manner. The total intensity $I_{liq.}$ of the density scattering in a liquid medium is proportional to its isothermal compressibility β_T. We therefore have

$$I_{liq} = C\left\{\beta_\phi + \left(\beta_T - \beta_\phi\right)\right\}.$$

If we now connect the Brillouin components with the adiabatic compressibility β_ϕ alone by extending the sound wave idea and the central component with the rest, the ratio of both the outer components put together to the centre should be $\beta_\phi : \beta_T - \beta_\phi$. Since the compressibilities β_ϕ and β_T are proportional to the specific heats C_v and C_p respectively, we see that the intensities of the three components should have the ratio $\frac{C_v}{2} : C_p - C_v : \frac{C_v}{2}$.

Closely connected with this phenomenon is the appearance of unresolved wings on either side of the Rayleigh line in liquids. Much work has also been done in this connection by Rousset, Rao and others. The principal experimental results are as follows. In all the liquids studied, the intensity of the rotation wing is a maximum at or very near the centre and falls off somewhat rapidly in the beginning but only gradually at larger distances. In all these respects, the phenomenon in liquids differs markedly from that in gases and from the predictions of

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[1] Physikal. Z. d. Sowjetunion, *5*, 172 (1934).

[2] Physikal. Z., *39*, 80 (1938).

the existing theories when applied to liquids. The wing extends much further than can be accounted for on the hypothesis of the rotating molecule exchanging energy with the light quantum. No appreciable changes take place in the distribution of intensity within the wing, even when the liquids are heated to the vicinity of their boiling points. The interpretation of these results is somewhat complicated on account of the difference of opinion that exists in regard to the origin of these wings.

Specific Heats in Relation to Raman Effect Data.—The unresolved wings obtained in liquids alongside the Rayleigh lines are replaced by broad bands when the Raman spectra of such substances are studied in the solid state. This striking observation, first made by Gross and Vuks in a few typical cases, was soon extended to a number of organic substances. On the other hand, the lattice oscillations that are observed in inorganic crystals such as $NaNO_3$, etc., are replaced by continuous wings, which are exactly similar to those that occur in liquids at ordinary temperature, when the crystals are melted. The nature and origin of these broad bands in the solid state, their relationship to the unresolved wings obtained with the same substance above its melting point and the exact mechanism by which the transition from the separate bands to a continuum takes place are not very clear and have been the subject of some discussion. It is, however, obvious that they are in some way related to the solid state and, being frequencies actually observed, should enter into the calculation of that part of the specific heat of the substance which arises from the translational and rotational degrees of freedom. On the other hand, the vibrational Raman frequencies will contribute to the other part of the specific heat arising from the internal degrees of freedom.

Since the discovery of the Raman effect, various attempts have been made to utilize the observed Raman frequencies for the purpose of explaining the specific heats of substances. The procedure is quite straightforward in the case of gases and vapours and a large number of examples have been worked out by Fowler[1]. Application to liquids is somewhat complicated

[1] *Statistical Mechanics*, 2nd Edn. (1936).

and mention may be made here of the work of Andrews and Southard,[1] Paramasivan[2] and Bhagavantam[3] in this connection. The subject may be broadly divided into two distinct parts: one relating to the specific heats at low temperatures and the other to the specific heats at the room temperatures. In the former case, the major part of the specific heat is explained with the help of the Debye theory and the investigation should therefore proceed on the lines of ascertaining the exact relationship, if any, between the Debye elastic spectrum and the low frequency oscillations recorded in the Raman scattering by solids and referred to above. Much progress has not been made in this direction. On the other hand, at comparatively high temperatures, all Debye functions based on low frequencies reach their limiting values and therefore the exact frequencies on which they are based are not of much significance. The contribution from internal frequencies, however, becomes appreciable at these temperatures and a full knowledge of these is necessary to predict the specific heat and its variation with temperature. Results of such calculations made in benzene, carbon tetrachloride and carbon disulphide are given below.

The contribution to specific heat on account of the six degrees of freedom (3 translational and 3 rotational) is taken as $6RD\left(\frac{\theta}{T}\right)$ at T where $\theta = 150$ in benzene. The exact relationship between the Debye limit corresponding to $\theta = 150$ and the observed low frequency Raman lines in solid benzene is not clear. Good reasons for the choice of this value are, however, given by Lord, Ahlberg and Andrews[4]. As has already been mentioned, its exact value is not of much significance when we are dealing with comparatively high temperatures. The internal frequencies of the benzene molecule are assumed to be 406(2), 538(1), 606·4(2), 670(1), 849·7(2), 992·6(1), 1008(1), 1025(2), 1145(1), 1160(2), 1176·0(2), 1190(1), 1477(2), 1520(1), 1595(2), 1854(1), 3048·3(2), 3061·5(1), 3063(1), 3077(2). The

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[1] Phys. Rev., *35*, 670 (1930).

[2] Ind. Jour. Phys., *6*, 413 (1931).

[3] Proc. Ind. Acad. Sci., *7*, 245 (1938).

[4] Jour. Chem. Phys., *5*, 649 (1937).

number in the bracket in each case represents the degeneracy of the corresponding oscillation and the total number of degrees of freedom comes out as 30 as it ought to. To each of these is assigned an Einstein function, and the aggregate specific heat is calculated alternatively in accordance with (2) and (3) which respectively give the specific heats of solid and vapour benzene.

$$C_v = 6RD\left(\frac{\theta}{T}\right) + \sum_{i=1}^{i=30} RE\left(\frac{h\nu_i}{kT}\right) . \qquad .. \quad (2)$$

$$C_v = 3R + \sum_{i=1}^{i=30} RE\left(\frac{h\nu_i}{kT}\right) . \qquad .. \qquad .. \quad (3)$$

In the case of CS_2 and CCl_4, we shall assume similar equations. The first term of (2) may be put equal to 12 calories in CCl_4. In CS_2, it should be taken as 10 calories, as out of a total of 9 degrees of freedom, only 5 are taken over by the lattice, the other 4 being internal. The vibrational frequencies in these cases and their degeneracies are given below.

CCl_4: 217(3), 313(2), 459(1), 777(3).

CS_2 : 397(2), 655(1), 1523(1).

TABLE LV

Specific heat of Liquid Benzene at Constant Volume

Temperature °C.	Contribution of the lattice	Contribution of internal frequencies	Total calc. as if it were a solid	Total calc. as if it were a gas	Observed Mills and McRae *	Observed Williams and Daniels †
0	11·72	9·68	21·40	15·68	21·15	..
20	11·76	11·01	22·77	17·01	22·09	21·57
40	11·78	12·44	24·22	18·44	23·00	23·13
60	11·80	13·83	25·63	19·83	24·06	25·22
90 (vapour)	..	16·0	..	22·0	23·4 ‡	..

* Jour. Phys. Chem., *14*, 797 (1910) and *15*, 54 (1911).

† Jour. Amer. Chem. Soc., *46*, 903 (1924).

‡ Observed C_p is taken from I.C.T. and C_v obtained therefrom by subtracting 2 calories.

TABLE LVI

Specific heat of Liquid CCl_4 at Constant Volume

Temperature °C.	Contribution of the lattice	Contribution of internal frequencies	Total calc. as if it were a solid	Total calc. as if it were a gas	Observed Mills and McRae * and Williams and Daniels †
0	12	11·53	23·53	17·53	21·24
20	12	12·05	24·05	18·05	21·50
40	12	12·52	24·52	18·52	21·69
60	12	12·94	24·94	18·94	22·41
80	12	13·32	25·32	19·32	22·82

* Jour. Phys. Chem., *14*, 797 (1910) and *15*, 54 (1911).

† Jour. Amer. Chem. Soc., *46*, 903 (1924).

TABLE LVII

Specific heat of Liquid CS_2 at Constant Volume

Temperature °C.	Contribution of the lattice	Contribution of internal frequencies	Total calc. as if it were a solid	Total calc. as if it were a gas	Observed Regnault *
0	10	3·64	13·64	8·64	11·70
20	10	3·89	13·89	8·89	11·70
40	10	4·12	14·12	9·12	11·77
97 (vapour)	..	4·66	..	9·66	9·95†

* Mem. de L' Acad., *26*, 262 (1862).

† C_p is taken from I.C.T. and C_v obtained therefrom by subtracting 2 calories.

In the above Tables, the observed values of C_v for benzene are obtained from the work of Mills and McRae and Williams and Daniels. These authors have given C_p at different temperatures and C_v is calculated therefrom by reducing it in the ratio of the adiabatic and isothermal compressibilities as determined by Tyrer. The following features of the results may be noted. The agreement, between the calculated and the observed specific heats, is very satisfactory in the case of benzene and CS_2 vapours. The specific heat observed in the vapour state is less than that obtained in the liquid. In all the three cases, the observed

specific heats for the liquid state at all temperatures lie between those calculated on the one hand, by treating the liquid as a solid and on the other, by treating it as a gas. In the case of benzene, the observed values are much closer to the solid values than in the other two cases where they are midway between the two sets of calculated values.

These results may be interpreted as follows. The thermal motion of liquid molecules, which goes to make up its heat content, is neither wholly disorganized in the form of random movements as in a gas nor wholly organized in the form of elastic waves as in the case of a solid. This important conclusion regarding the nature of the liquid state has already been indicated in the earlier section.

Change of State and Dipole Moments.—Tables LVIII and LIX contain the Raman frequencies in a few cases which have been studied in different states of aggregation. Only the prominent frequencies are included in the case of polyatomic molecules.

TABLE LVIII

Dependence of Raman Frequencies on the Nature of Aggregation : Non-polar Molecules

State \ Gas	H_2	O_2	N_2	CO_2	N_2O	CS_2
Solid ..	..	..	..	1285, 1388	..	653
Liquid ..	4158	1552	2330	1283, 1387	1281, 2223	655
Gas ..	4156	1556	2331	1286, 1389	1284, 2224	655
Solution ..	..	..	..	..	....	..

It is very clear that the variations are none at all or very insignificant amongst the substances contained in Table LVIII, whereas the variations in Table LIX are quite prominent in several cases. The obvious conclusion to be drawn is that when polar molecules are more closely packed, their internal frequencies are affected. With the exception of HCN, the frequency in the liquid state is always less than that obtained in the gaseous state. Braune and Engelbrecht[1] have suggested

[1] Z. f. Phys. Chem. (B), *19*, 303 (1932).

TABLE LIX

Dependence of Raman Frequencies on the Nature of Aggregation : Polar Molecules

State \ Gas	NH_3	H_2O	H_2S	SO_2	HCl	HBr	$HgCl_2$	$HgBr_2$	HCN	PCl_3	$ASCl_3$	$SbCl_3$	$AsBr_3$	D_2O
Solid ..	..	3394	..	..	2760	2465	312	..	..	..	..	338	..	..
Liquid ..	3300	3453	2578	1145	2778	2487	314	195	2096	511	405	360	273	2515
Gas ..	3334	3654	2615	1154	2880	2558	355	220	2089	523	422	382	287	2666
Solution ..	3310	..	..	1136	..	..	331	205	..	..	..	..	..	..

that the percentage differences in the frequencies in the vapour and the liquid states are approximately a linear function of the dipole moment.

Transition from crystalline to amorphous state is another case of great interest and it is well illustrated by the example of quartz. There is a general correspondence between the Raman spectra obtained in crystalline quartz and the fused variety but the lines in the latter are somewhat diffuse. It is a common feature of all amorphous substances that they exhibit broad and diffuse bands. A large number of glasses of varying compositions have been examined and found to exhibit only weak and diffuse bands.

Polymorphous Crystals.—Raman spectra of different modifications of crystals are studied in a few cases. We may expect the low frequency oscillations to undergo appreciable alterations as they are most sensitive to any changes that may be produced either in the lattice or in the freedom of movement possessed by the molecules within the lattice. The results are given in Table LX.

Data for the chloro- and bromobenzenes are from Sirkar and Gupta [1] and for sulphur and calcite from Venkateswaran [2] and Bhagavantam [3] respectively. With the help of X-rays, Sirkar has shown that the alterations produced in *p*-dichlorobenzene are not accompanied by any marked changes in the lattice. The oscillations of sulphur do not show any prominent changes as we go from the rhombic variety to the monoclinic. This is probably to be ascribed to the fact that with the exception of the lowest, they are all internal frequencies of the S_8 molecule. In the case of calcite and aragonite, marked changes occur both in the positions and the relative intensities of the lattice oscillations. This is in accordance with what may be expected as the lattice itself is changed from one symmetry type to another.

Electrolytic Dissociation.—One of the most fruitful applications of Raman effect has been the determination, with its

[1] Ind. Jour. Phys., *10*, 473 (1937).
[2] Proc. Ind. Acad. Sci., *4*, 345 (1937).
[3] Z. Krist., *77*, 43 (1931).

TABLE LX

Raman Lines in Different Modifications of Crystals

Substance	Temperature °C.	Conditions of expt. or crystal symmetry	Frequencies	Remarks
p-dichlorobenzene	45	Melted and gradually cooled to 45°C.	40 (2) 50 (2) 82 (2*bd*)	....
	32	Do. 32°C.	40 (2) 50 (2) 82 (2*bd*)	
	32	Above mass once cooled in ice	46 (2) 50 (2) 92 (2*d*)	
p-dichlorobenzene	180	Solid kept in liquid air	55 (2) 60 (2) 105 (2*s*)	....
p-dibromobenzene	32	Melted, solidified and cooled to 32°C.	36·0 (3) 93 (2*d*)	....
	-40	Solid kept in liquid ammonia	37·5 (3) 95 (2*d*)	
	-180	Do. air	42 (3) 104 (2*s*)	
Sulphur	25	Orthorhombic ..	88, 114, 152, 185, 216, 243, 434, 468	
	110	Monoclinic	80, —, 152, —, 216, —, —, 470	No striking variations
Calcite ..	30	Hexagonal ..	156 (5) 283 (10)	There are small changes in some of the internal frequencies
Aragonite ..	30	Orthorhombic ..	113 (2), 154 (10*d*), 182 (2), 208 (5), 246 (1), 261(1)	Principal line of CO_3^- remains constant

help, of the degree of dissociation of certain substances such as nitric acid, sulphuric acid, etc., in aqueous solutions of different concentrations. If we take a molecule like HNO_3, it is clear that the Raman spectrum of the molecule as such will be different from the Raman spectrum obtained from a NO_3 ion. If the Raman spectra of aqueous solutions of HNO_3 are obtained at different concentrations, after allowing for the dilution, the variations in intensity of any prominent line characteristic of either the HNO_3 molecule or the NO_3 ion may be utilized for obtaining the rate at which the concentration of the NO_3 ions is progressively increasing with increasing dilution. The strong line at about 1050 due to the NO_3 ion has been chosen by Rao [1]

[1] Proc. Roy. Soc., *127*, 279 (1930).

for this purpose and he obtained the results shown in Figs. 35 and 36.

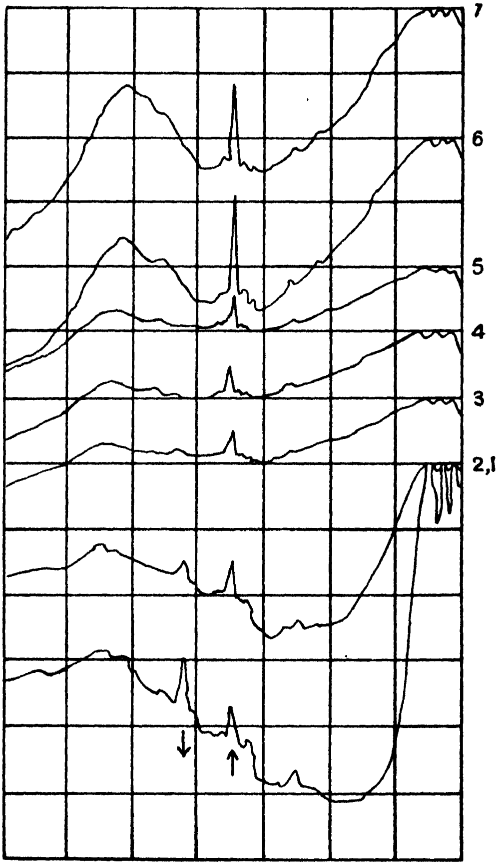


FIG. 35.

Fig. 35 contains the microphotometric records of the Raman spectra of aqueous solutions of nitric acid. The concentration of the acid decreases as we proceed from curve number 1 to curve number 7. The maxima, marked by the downward arrow, correspond to the undissociated HNO_3 molecule. Those denoted by the upward arrow correspond to the NO_3 ions. Fig. 36 shows the relation between the concentration of nitric acid and the degree of dissociation. Curves 1, 2 and 3 in this

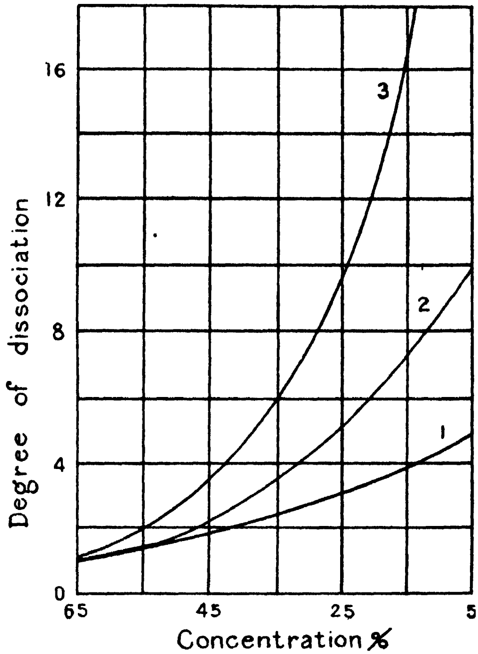


FIG. 36.

figure are obtained respectively from the viscosity-conductivity formula, Kohlrausch's conductivity formula and intensity measurements of the Raman line at 1050 due to the NO_3 ion. The departures between the results obtained with the help of the viscosity-conductivity data and Kohlrausch's conductivity formula and those obtained from Raman effect are ascribed by Rao to the inapplicability of standard methods to measure the true degree of dissociation even at moderate concentrations.

Similar investigations on aqueous solutions of sulphuric acid by Woodard and Woodward and Horner have shown that in such solutions, H_2SO_4 ionizes into HSO_4 and SO_4 ions whose concentration increases progressively with dilution. They had chosen 908, 1048 and 982 as the typical lines arising respectively from H_2SO_4, HSO_4^- and SO_4^{--} and their curves are shown in Fig. 37. In this figure, these typical lines are respectively represented by the letters C, F and E. The production of HSO_4

ions is obviously the first step in the ionization process. On further dilution, SO_4 ions are produced and the lines due to SO_4 begin to appear and gain in intensity.

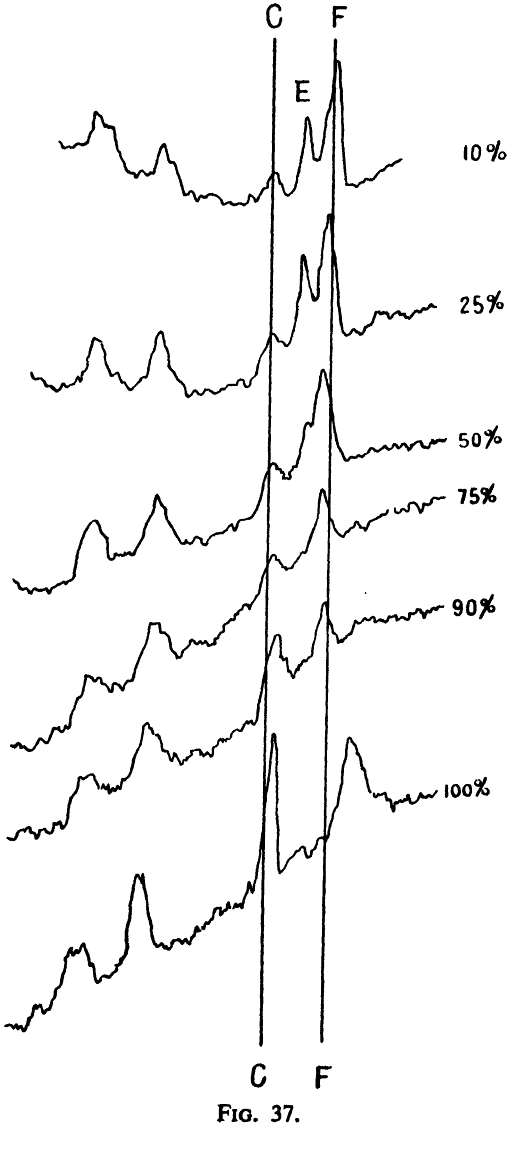


FIG. 37.

The next case of some interest is that of H_2SO_3 and this has been studied by Fadda,[1] Nisi[2] and others. Besides the detection of the HSO_3 ion, one of the most interesting observations made in this case is the recording of lines due to free SO_2. A large amount of SO_2 appears to be present as dissolved gas in water. Aqueous solutions of many other acids, such as HCl, H_2F_2, iodic acid, perchloric acid, phosphoric and phosphorus acids, selenic acid, selenious acid, have been studied with similar results. Amongst the more important and well-established results, the following may be noted. In the case of HCl solutions, no Raman lines are recorded and we have to conclude that there is complete ionization. Aqueous solutions of H_3PO_4 ionize into H_2PO_4 ions first and then into HPO_4 ions later. On further dilution, PO_4 ions are produced. Solutions of selenic acid ionize into $HSeO_4$ ions and the latter ionize on further dilution into SeO_4 ions. The second stage begins only at 50% and is not very appreciable even at 7·5% dilution. Selenious acid is found to behave in a more normal manner when compared with sulphurous acid and dissociates into SeO_3 ions to a small extent. Iodic acid is found to ionize progressively and the ionization is accompanied by a polymerization of IO_3 into I_2O_6.

Hydrolysis.—The problem of hydrolysis is quite similar to the case of electrolytic dissociation. If a salt, which possesses a Raman spectrum different from either the base or the acid, is hydrolyzed by the addition of water, it is easily seen that by measuring the relative intensities of a set of lines characteristic of either the base, the salt or the acid, the degree of hydrolysis can be estimated. Practical considerations limit, however, the applicability of such investigations to cases where the extent of hydrolysis is fairly large.

Krishnamurti[3] has shown that the Raman spectra of aqueous solutions containing hydrochlorides of weak bases such as urea and hexamine show certain lines characteristic of the base in addition to those of the hydrochloride. These are

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[1] Nuovo Cimento, *9*, 168 (1932).
[2] Jap. Jour. Phys., *6*, 1 (1930).
[3] Ind. Jour. Phys., *6*, 345 (1931).

attributed to the formation of the base by hydrolysis. The relative intensities of these two sets of lines give an idea of the degree of hydrolysis. In this way, he found that urea hydrochloride is not appreciably hydrolyzed in a 4N solution. The hydrolysis becomes appreciable in a 2N solution and much more so in a normal solution. He also concluded that the hexamine base is only about one-third as strong as the urea base.

Common Ion Effect.—The common ion effect consists in repressing the ionization of a molecule, by adding to the solution a suitable substance having the same anion as the original substance, and thus producing an excess concentration of the anions. If the original molecule has characteristic Raman lines, which are distinct from those produced by the constituent ions, the degree of ionization at all stages may be followed as has already been shown. We should thus be able to observe an abnormal increase in an otherwise progressively decreasing intensity of the line by adding the repressing agent at some stage of dilution. Hibben [1] has chosen the example of an aqueous solution of $ZnCl_2$. In concentrated solutions, a Raman line at 275 is recorded and this gradually disappears with increasing dilution as neither zinc nor the chlorine ions can be responsible for this line. The addition of NaCl to such a solution will obviously produce a large number of chlorine ions and the common ion effect should be expected to set in. The ionization of $ZnCl_2$ should be repressed and the Raman line at 275 due to the molecule should accordingly pick up in intensity. These expectations are confirmed in a very striking manner by the results of Hibben. The curves obtained by him are reproduced in Fig. 38.

In curves 4 and 5, the $ZnCl_2$ line shows a remarkable increase in intensity although the concentration of $ZnCl_2$ is very low. Due to the repressed ionization, the proportion of unionized $ZnCl_2$ molecules in these cases is evidently even larger than that obtained in 1 molal solutions (curve No. 1). Hibben has further studied the effect of forming an excess

[1] Jour. Chem. Phys., *5*, 710 (1937).

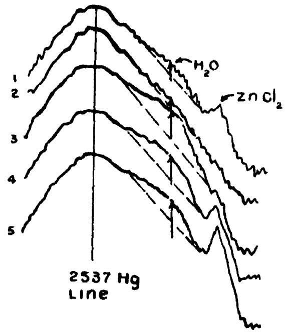


FIG. 38.

number of common kations in the solution. He found that in such a case, there is no appreciable repression of ionization. This conclusion is based on the result that the addition of $ZnSO_4$ to the above solution, at various stages of dilution, causes no marked increase in the intensity of the $ZnCl_2$ line.

CHAPTER XVIII

RAMAN EFFECT IN RELATION TO ORGANIC CHEMISTRY

General Introduction.—From the point of view of organic chemistry, a study of the Raman effect has been of great value. It has thrown considerable light on a variety of problems. Amongst the major fields in which it has been successfully utilized are: (i) the determination of the presence or absence of specific linkages in a molecule, (ii) qualitative identification of impurities of certain types, (iii) quantitative estimation of the relative proportions in which the constituents of a mixture are present, (iv) the elucidation of structures of important molecules like benzene,[1] and (v) a study of different types of isomerism. The field of research and the results obtained are so vast that it is not possible to do complete justice here to this branch of the subject.[2] Only the more important aspects are dealt with and no attempt is made to present an exhaustive collection of the results obtained with the numerous substances so far investigated. A brief and general review will first be given of the common groups of substances studied and the linkages that usually occur, laying emphasis on the notable points, if any, in relation to each one of the groups or linkages. Some special aspects including those mentioned above will then be dealt with.

Saturated Hydrocarbons.—Normal Saturated hydrocarbons up to $C_{12}H_{26}$ and some of their isomers have been studied. The accompanying chart, taken from Hibben, gives an idea of the increasing complexity of the Raman spectrum as we pass from the simpler to the more complicated members. The frequencies may be broadly divided into 4 ranges. Those which lie in the regions 800 to 1100 and 200 to 800 may respectively be attributed to longitudinal and transverse oscillations of the C—C linkages.

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[1] This has already been discussed in chapter XIII.

[2] For a very exhaustive discussion, reference may be made to J. Hibben, *The Raman Effect and Its Chemical Applications* (1939).

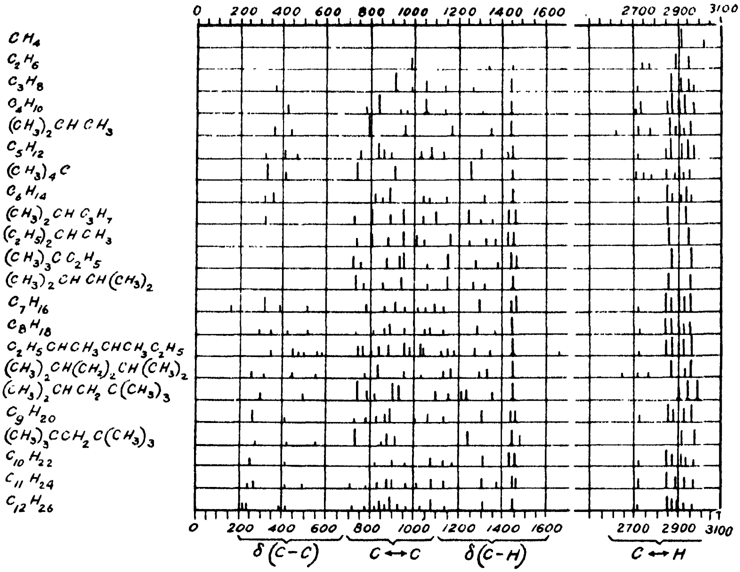


FIG. 39.

Similarly the regions 2700 upwards and from 1100 to 1460 may be taken to represent the corresponding oscillations of the C—H linkages.

Halogen Derivatives of the Paraffins.—The introduction of a halogen often causes new lines to appear in the region below 800. The primary frequencies attributable to the C—Cl, C—Br and C—I linkages are respectively in the neighbourhood of 700, 600 and 500.

Unsaturated Hydrocarbons.—Under this class of substances, the olefines, the di-olefines, and the acetylenes may be dealt with. Several of these compounds have been studied and most of them show very prominent lines. The characteristic frequencies of the C = C, C = C = C and C ≡ C linkages

are 1650, 1100 and 1960 to 2250 respectively. The variations which these shifts undergo from substance to substance are of great interest and these will be dealt with later. The case of $C = C$ and a study of the variation of its characteristic frequency from structure to structure have been of particular utility in problems relating to the constitution of molecules like the terpenes and related compounds. The lines noted above are sometimes very intense and, as will be seen later, they may be utilized for the purpose of identifying small percentages of impurities containing the corresponding linkages. The fact that the ethylenic linkage occurring in a molecule of the type $R_1R_2C = CH_2$ has a frequency of about 1650, which is less than 1680 exhibited by structures of the type $R_1R_2C = CHR$ in which a further substitution takes place, has found an interesting application. The two isomers, rhodinol and citronellol, having the formulae (1) and (2) respectively belong to these two types.

$$CH_2OH-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}} = CH_2$$

Type $R_1R_2C = CH_2$ .. .. (1)

$$CH_2OH-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_2-CH = \underset{\displaystyle CH_3}{\underset{|}{C}}-CH_3$$

Type $R_1R_2C = CHR$ .. .. (2)

Ordinary citronellol gives a strong line at 1677 which is accompanied by a faint line at 1645. It is concluded from this result that in this substance, although citronellol predominates, rhodinal also is present to a small extent.

Alcohols.—A series of alcohols have been studied. The lines at 1030 in methyl, 885 in ethyl, 856 in propyl and 825 in butyl alcohols are characteristic of the C—O linkage. Most of the alcohols give a broad band with a maximum near 3400 and this may be attributed to the O—H linkage. The intensity of scattering in these liquids is usually very low. Amongst the polybasic alcohols, glycerine is of special interest and its Raman spectrum has recently been studied with great care.[1] Some of

[1] B. D. Saksena, Proc. Ind. Acad. Sci., *10*, 333 (1939).

the sugars have also been studied but the lines recorded are not many in number, if we consider the complexity of these molecules. The inherent weakness of the scattered light and the continuous spectrum arising from inevitable impurities are partly responsible for this. Improved technique appears to be necessary for a complete study of these substances and the results are likely to be of value from the point of view of the constitution of sugars.

Ethers, Thio-ethers and Mercaptans.—Generally, the Raman spectra of ethers resemble those of the corresponding hydrocarbons or the alcohols. The introduction of sulphur gives rise to new frequencies as in the case of a halogen and also considerably increases the scattering power of the substance. The C—S linkage gives lines in the region of 650 and the S—H in the region of 2580. All mercaptans give two strong lines corresponding to the above linkages.

Aldehydes, Ketones and Oximes.—With a few exceptions, all aldehydes show a characteristically strong line at about 1720, which may be attributed to the carbonyl group. Its absence in certain cases, such as para-formaldehyde, paraldehyde and aqueous solutions of formaldehyde of only moderate concentrations, is obviously due to the special conditions that prevail. Para-formaldehyde and paraldehyde are polymers and do not contain the $C = O$ group at all. If only moderate quantities of formaldehyde are present in aqueous solutions, it is possible that the whole of it exists in the form of methylene glycol $CH_2(OH)_2$.

The important group in ketones is again the $C = O$ group. Its behaviour is more or less similar to that obtained in aldehydes.

A few aldoximes and ketoximes have been studied by Bonino and Manjoni-Ansidei and they have discussed their results in relation to the structure of oximes. All the aliphatic oximes give a prominent line at about 1660 and the aromatic oximes at about 1630. This is attributed to the $C = N$ linkage. This result, when taken along with the fact that there are no lines that may be attributed to the $N = O$ linkage, furnishes evidence

in favour of the ordinarily accepted constitution

$$\begin{array}{c} R-C-R' \\ \| \\ H-N\rightarrow O \end{array}$$

for the oximes. Bernstein and Martin[1] have also recently studied the Raman spectra of some oximes.

Acids and their Derivatives.—In common with the aldehydes and ketones, these exhibit strong lines in the region of 1700 due to the $C = O$ group. In the lower members of the series such as formic and acetic acids, the lines obtained are usually not sharp. This result may be attributed to the fact that they are highly associated liquids. A few acid chlorides, anhydrides, amides, etc., have been studied. The anhydrides have the peculiar property of giving two lines in the region of the $C = O$ frequency. They are, however, somewhat high and occur at about 1770 and 1840 respectively. Amongst the dibasic acids studied, mention may be made of oxalic, malonic, tartaric and citric acids. In these acids, the carbonyl frequency does not come out so readily as in monobasic acids.

Esters and Acid Salts.—A large number of esters have been studied. A few metallic acetates, formates, etc., have also been studied. One noteworthy feature in the spectra of these compounds is that the $C = O$ frequency is present only feebly.

Cyanogen Compounds.—Both the HCN gas and the liquid show a strong line at about 2090. This value is quite close to that obtained for the $C \equiv C$ and other linkages involving triple bonds. We have, therefore, to conclude that the carbon and nitrogen in HCN are linked by a triple bond. Besides this prominent line, a weak satellite at 2069 has also been observed in the HCN liquid. This has been attributed to the isomer $H-N \overrightarrow{\equiv} C$. Dadieu and Kohlrausch have estimated, from the relative intensities of these two lines, that $H-N \overrightarrow{\equiv} C$ is present ordinarily to the extent of about $\frac{1}{2}\%$. All other organic nitriles and isonitriles studied have been found to give shifts of this order. The isonitriles usually give a lower shift and this fact has been utilized to differentiate between the two isomers. Similarly, some thiocyanates and isothiocyanates have been

[1] Trans. Roy. Soc. Canada, *31*, 105 (1937).

investigated. Ethyl thiocyanate gives 2152 whereas the corresponding isothiocyanate gives a lower shift 2106.

Benzene and its Derivatives.—Benzene has been investigated very extensively. A very large number of derivatives have also been studied. The Raman spectrum of benzene, in relation to its constitution, has already been considered very fully. Amongst the lower oscillation frequencies in benzene, 606, 849, 992 and 1178 appear to be very characteristic of the hexagonal ring and they continue to appear in practically all the derivatives with slight variations. The effect of substitution in benzene in all its aspects, such as monosubstitution, disubstitution, etc., and in the latter case different alternatives such as ortho, para, meta, have all been studied in great detail by Kohlrausch, Andrews and co-workers.

Saturated Cyclic Compounds, Cyclo-olefines and Polycyclic Compounds.—The parent members of the saturated cyclic compounds have been studied up to cyclo-octane. Each ring has a characteristic line which persists in all the corresponding derivatives with slight alterations. The value of this frequency is 1187 in cyclopropane, about 920 in cyclobutane, 890 in cyclopentane, 800 in cyclohexane, 730 in cycloheptane and 700 in cyclo-octane.

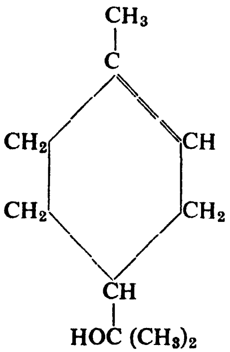
A number of cyclo-olefines such as cyclopentadiene, cyclohexene, cyclopentene, etc., and their derivatives have been studied. The ethylenic linkage in cyclopentadiene exhibits a rather low frequency, namely 1500. In cyclopentene, cyclohexene, cycloheptene and cyclo-octene, it is 1615, 1650, 1651 and 1604 respectively.

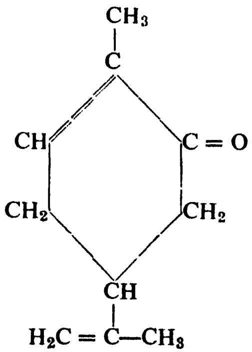
Amongst the more important polycyclic compounds studied, are naphthalene, dekalin and tetralin. Many of their derivatives have also been studied. The low frequencies that are characteristic of the naphthalene structure are 512, 758, 1024, 1149 1382 and 1573.

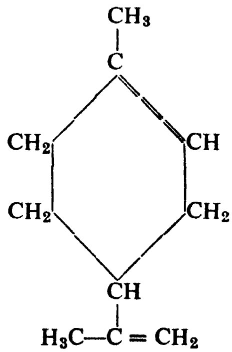
Heterocyclic Compounds.—Amongst the substances studied under this class of compounds, furan and its derivatives, pyrrole and its derivatives, pyridine, piperidine, thiophene, etc., may be mentioned. The spectra obtained are usually very intense, complicated and difficult of interpretation. The frequencies

characteristic of specific linkages are considerably shifted. As an example, we may mention the occurrence of the frequency due to the C = C linkage at as low a value as 1500 in furan and its derivatives. In some cases, they are so changed that it is difficult even to identify them.

Terpenes.—Terpenes, analogous compounds and isomers have been very extensively investigated both from the point of view of their constitution and the detection of particular types in naturally occurring mixtures. The subject is intimately connected with the behaviour of the C = C and C = O linkages with varying conditions. The relevant features in respect of these linkages are given in a following section. With the help of these and from a knowledge of the C = C and C = O frequencies occurring in a particular derivative, it is possible to say whether the observed results are in agreement with the proposed constitution or not. As an example, we may take the case of terpineol which has the constitution given below.


Terpineol


Carvone


Limonene

This is analogous to methyl cyclohexene, in which the C = C has a frequency of 1675. We may also view the double bond present as belonging to the type $CHR = CR_1R_2$ and arrive at the same result, since the characteristic C = C frequency in such a group is 1675 (see Table LXII). In agreement with the above expectation, terpineol has a frequency of 1673. We may choose carvone as another example. This substance has the constitution given above. There are two C = C bonds, one

being external and the other internal to the ring. The internal bond is conjugated with a ketonic C = O link and we see from Table LXII that we should expect a frequency of 1638 for this link. Carvone shows a line at 1646. The external double bond is of the type CH_2=CRH and the value expected, as will be shown in the next section, is 1650 which is close to 1646.

Two separate frequencies for the internal and external C = C bonds are not observed in carvone, presumably because of their nearness to each other. We may take another instance, namely limonene, where they are well separated. Limonene has the constitution given above and possesses one internal and one external C = C bond. The internal one is again similar to that obtained in methyl cyclohexene or R_1R_2C = CHR type and we should expect a frequency of 1675 for this. The external one is of the type H_2C = CR_1R_2 and we should accordingly expect a frequency of 1650. Limonene actually gives two frequencies at 1680 and 1658 in agreement with our expectations. All the terpenes and terpenoid compounds may be treated in this manner in the light of their chemical constitution. Table LXI is reproduced from Hibben's work and refers to a few terpenes treated in this manner. The. C = O link is also dealt with similarly with the help of the figures given in Table LXII.

The agreement in most cases is very satisfactory. Amongst the other important results obtained with terpenes, the following may be mentioned. Essence from *Pinus longifolia* has been analyzed by the Raman spectrum method and found to contain two forms of carene, namely Δ^3-carene and β carene. Successive distillates from the oil of indienne show the presence of pinene, β pinene, and Δ^3-carene. Distillates from the essence of citronel of Java similarly show pinene, β pinene, limonene and other terpenes. The chief constituents of several other essential oils have also been identified by the Raman spectrum method. Numerous other results of importance have been obtained and a reference has to be made to the original papers for a fuller account. It must, however, be mentioned here that one must be cautious in extending the above arguments too far, as the constitutive influences can always be estimated from alternative

TABLE LXI

Calculated and Observed C = C and C = O Shifts for Some Terpenes

Compound	Observed frequency		Calculated frequency	
	C = C	C = O	C = C	C = O
Pulegone ..	1617	1673	1600	1670
Carvenone ..	1632	1673	1638	1670
β-Thujone ..	..	1688 or 1750	..	1712
Menthone ..	..	1714	..	1712
Fenchone ..	..	1731	..	1712
Terpineol ..	1675	..	1675	
Carvone ..	1646	1673	1638	1670
α-Pinene ..	1656	..	1675	..
l-Limonene ..	1658	..	1650	..
	1680	..	1675	
Sabinene ..	1650	..	1650	..
Menthene ..	1673	..	1675	..
Geranial ..	1647	1681	1640	1689
			1678	
Citronellal ..	1675	1719	1650	1720
Citronellol ..	1675	..	1650	
Linalool ..	1672	..	1678	
	1646	..	1640	
Geraniol ..	1675	..	1678	

view-points thus leading to slightly different results. The large discrepancies that exist between the results of various workers in this field, to which attention has recently been drawn by Angus,[1] have also to be borne in mind in this connection.

Miscellaneous.—A number of other substances, not mentioned above, such as organo-metallic compounds, amines, amides, imido compounds, unsaturated nitrogen ring compounds, vegetable oils, etc., have been studied. The purpose of such investigations in most cases has been to get some information with regard to the chemical constitution.

C—H Linkage.—The shifts corresponding to this linkage are large and may be only a few or several in each molecule depending upon its complexity. They usually lie in the region 2800 to 3400. Sometimes, one or more lines also appear in the region

[1] Proc. Ind. Acad. Sci., *8*, 529 (1938).

of about 1450 which may also be attributed to this pair. Approximate values of C—H frequency, obtained under various conditions, are given below.

C—H (aliphatic)	2918
C—H (aromatic)	3054
$C—CH_3$	2930 / 2862
$C—CH_2—C$	2970
CH_2 (transverse)	1450

The above values are to be regarded as only the averages or the most probable ones. There are stray cases where the departures from the above figures are considerable.

C—C Linkage.—The principal line attributable to this linkage is in the neighbourhood of 990. In ethane, the corresponding frequency is 993. With increasing length of the chain, this value becomes less and less and more lines develop. Fig. 39 shows these features.

C = C Linkage.—This is one of the most important and very widely studied links. Without extensively quoting the results, the main features will be stated serially. The frequency has a value of 1620 in ethylene. In compounds of the type $CH_2 = CHX$, where X is either a hydrocarbon radical or a carboxyl group, the frequency increases to about 1650 or a little less. If X is a halogen or an aldehydic group, the frequency diminishes. If the substitution is in a β position with respect to the double bond, the effect is not so marked as it is when the substitution is in an alpha position. Disubstitution may take place in two different ways, both the substituted groups being attached to one carbon atom in one case and distributed to both in the other. We accordingly have molecules of the type $CH_2 = CR_1R_2$ or $CHR_1 = CHR_2$.[1] In the former type, the frequency is in the neighbourhood of 1650 and in the latter, it is about 1660 or 1675 according as the resulting molecule is of the *cis* form or of the *trans* form. Trisubstitution results in molecules of the type $CHR = CR_1R_2$ and the frequency in such molecules is further

[1] Geometrical isomerism is met with in this type of molecules and this aspect will be dealt with later.

enhanced to about 1675. Effect of conjugation by another double bond is to decrease the frequency. These and other influences are represented in a concise form in Table LXII. The shifts of the unsubstituted hydrocarbon are given in brackets. The type of linkage whose shifts are being given for various surroundings is noted under column 1. If any linkage is given in column 2, the indication is that the linkage in column 2 is conjugated with that in column 1. When two shifts are paired, they refer to the two possible *cis* and *trans* isomers.

TABLE LXII

Influence of Substitution on C = C and C = O Linkages (Hibben)

Linkage		Hydrocarbon	Aldehyde	Ketone	Acid	Ester	Anhydride
			Aliphatic hydrocarbons				
1	2						
C = C		(1620) 1664-1678					
C = C	C = C	1634-1660					
C = C	C = O	. . .	1620 1647	1600	1638	1664 1679	
			1720	1705	1654	1735	
C = O	C = O	. .	. .	1725	1735	1735	1750, 1820
C = O	C = C	. . . .	1689	1668	.	1740	
			Cyclic Compounds				
			C_5				
C = C	. .	(1615) 1658					
C = C	C = C	1500					
C = C	C = O	. . . .	1616	. .	. .	1631	
C = O	. .	. . . .	. .	1735	. .	. .	
C = O	C = C	. . . .	1676	. .	. .	1715	
			C_6				
C = C	. .	(1650) 1675	. .	. .	. .	. .	
C = C	C = C	1576 1615-1635	. .	. .	. .	. .	
C = C	C = O	. . . .	. .	1638	. .	1672	
C = O	. .	. . . .	. .	1712	. .	1740	
C = O	C = C	. . . .	. .	1670	. .	1735	
C = C (benzene)	. .	(1584) (1605) 1604	1597	1597	1601	1602	
C = O	C = C (phenyl)	. . . .	1690	1677	1670	1724	
			C_7				
C = C	. .	(1651) 1672					
			C_8				
C = C	.	(1604)					

C ≡ C Linkage.—In acetylene, the frequency of this linkage is 1975. In monosubstituted compounds of the type RC ≡ CH,

it ranges between 2100 and 2120. In disubstituted compounds of the type $RC \equiv CR_1$, two frequencies occur, one in the range 2230 to 2240 and the other in the range 2300 to 2320.

C = O Linkage.—This linkage comes next in importance to C = C and is met with in a variety of organic compounds. The frequency that may be attributed to it is very often in the neighbourhood of 1720, although cases are known where it goes down as low as 1650 or as high as 1800. The lowest value occurs in acids. The frequency slightly increases when we come to ketones and more so in aldehydes. This frequency is also subject to constitutive influences similar to those noticed in the case of C = C linkage.

Application to Analysis of Mixtures.—Both qualitative and quantitative analysis of mixtures of organic substances with the help of Raman effect have been attempted. The fact that certain substances exhibit strong and characteristic Raman lines enables us to detect their presence even in minute quantities in a given sample. The following Table, taken from a recent paper by Goubeau [1], illustrates a few cases.

TABLE LXIII

Application of Raman Effect to Organic Analysis

Mixture	Percentage detected	Authors
Benzene in dioxane and *vice versa*	1 to 2%	Hanle and Heidenreich
Olefines in cyclopropanes ..	1·3%	Lespieau, Bourguel and Wakeman
Styrol in ethylbenzene ..	0·4%	Weiler
p-xylene in *m*- and *o*-xylene ..	0·5%	Birckenbach and Goubeau
Benzene in petroleum benzine and in CCl_4	0·1%	Goubeau

A few other mixtures, not included in the above Table, have also been studied. In principle, the method is applicable to any case provided the substance in question exhibits a characteristic

[1] Angewandte Chemie, *51*, 11 (1938).

and strong Raman line. It is well known to workers in this field that small quantities of impurities, present in a sample of another substance, often give their own lines in well-exposed Raman spectra.

Results of the application of Raman effect to a quantitative estimation of the constituents in a mixture are shown in Table LXIV. These are taken from Goubeau. Reference may also be made to the recent work of Andant[1] for further details in this connection.

TABLE LXIV

Application of Raman Effect to Organic Analysis

Benzene content				
In	Given	Measured	Error	Error expressed as % of benzene
Petroleum benzine ..	1·0	1·2	+0·2	+20·0
Do.	3·8	4·0	+0·2	+5·3
Do.	12·5	12·7	+0·2	+1·6
Do.	75·0	77·9	+2·9	+3·9
Toluene	80·0	78·3	−1·7	−2·1
Commercial motor benzene..	80·0	76·0	−4·0	−5·0

Isomerism in Organic Compounds.—Several cases of ordinary isomers such as the ortho-, meta- and para-disubstituted derivatives of benzene, primary, secondary and tertiary hydrocarbons or alcohols, etc., have been studied. Generally, as the whole structure changes from one isomer to the other, the entire symmetry and hence the Raman spectrum is considerably changed. That this is so in several cases may be seen from Fig. 39. As has already been mentioned, the isomerism of cyanides and isocyanides has been studied very completely. The results indicate that in both cases, carbon and nitrogen are bound by a triple bond. The structures are represented respectively as R—C$\equiv$N and R—N$\stackrel{=}{\rightarrow}$C. Cyanates, thiocyanates and

[1] Comptes Rendus, *206*, 1294 (1938).

their isomers have also been studied but the results are not conclusive.

Geometrical isomerism may be considered next. Three important aspects, namely the variation in the C = C frequency, general similarity or otherwise between the spectra of the isomers and the relationship between the polarization factors, present themselves here. In Table LXV are collected the

TABLE LXV

C = C Frequency in cis *and* trans *Isomers*

Compound	CHBr=CHBr	CHCl=CHCl	Crotonic acid	Methyl ester of crotonic acid	β-chloro crotonic acid	Dimethyl ester of maleic or fumaric acid	Diethyl ester of maleic or fumaric acid	Stilbene	2-pentene	2 octene	1-phenyl 1-propene
cis ..	1581	1587	1645	1644	1631	1650	1653	1630	1658	1658	1642
trans ..	1581	1577	1652	1655	1644	1650	1657	1632	1674	1673	1664

frequencies of the C = C linkage in a few *cis* and *trans* isomers that have been studied. With the exception of a few compounds, the frequency in the *trans* form is always definitely higher than that obtained in the *cis* form.

In general, the spectra are quite different and this is in accordance with what may be expected, since the symmetry of the molecule changes altogether from the *cis* to the *trans* variety. The polarization factors are also different. These are well brought out by the recent work of Paulsen, whose results for *cis* and *trans* dichloro-ethylenes are given in Table LXVI. The depolarization factors are given in brackets. When data are available for more than one exciting line, the mean value is given.

TABLE LXVI

Polarization of Raman Lines in cis *and* trans *Isomers* $\left(\begin{array}{c} CHCl \\ \| \\ CHCl \end{array}\right)$

Frequency and ρ for *cis*	175 (0·52)		405 (0·89)	564 (0·90)	711 (0·07)			1178 (0·68)		1587 (0·19)	3077 (0·25)
Frequency and ρ for *trans*		349 (0·29)				763 (0·69)	847 (0·09)		1270 (0·21)	1577 (0·10)	3070 (0·17)

These differences have been used for the purpose of following up the mutual conversion of one isomer into the other under certain physical conditions.

Several authors have studied the Raman spectra of a few acetoacetates with a view to elucidate the phenomenon of keto-enol isomerism. Whenever there is a possibility of an enolic form existing, a line attributable to C = C is observed. Besides the C = O line, which is usually greater than 1700 in these molecules, methyl acetoacetate, ethyl acetoacetate, methyl ethylacetoacetate respectively exhibit lines at 1626, 1656 and 1618. These are obviously due to the C = C linkage present in the enolic form. It is also easy to see that methyl dimethylacetoacetate cannot exist in two forms and accordingly no line in this region is observed in the Raman spectrum of this substance. Several other instances of isomerism, akin to the keto-enol type, have been discussed by Hayashi[1] and Kohlrausch and Pongratz.[2]

The Raman spectra of a number of optical isomers such as the *d* and *l* pinenes, camphors, borneols, camphoric acids, etc., have been obtained. No differences between the spectra of the two forms are detected in any case.

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[1] Sci. Papers Inst. Phys. Chem. Research Tokyo, *21*, 69 (1933).

[2] Monatsh, *70*, *3/4*, 226 (1937).

Appendix I

RADIATION FROM MOVING CHARGES

Radiation from an Accelerated Charge.—If a charge e is situated at the centre of a sphere of radius r and is moving with an acceleration f parallel to the Z axis, it will radiate energy at a rate which may easily be calculated on the basis of the electromagnetic theory of light. The electric and magnetic fields at any point P on the surface of the sphere (Fig. i) are given by $E = H = \frac{e \sin\theta . f}{c^2 r}$.

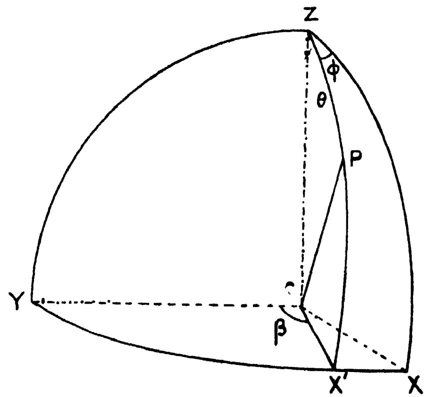


Fig. i.

θ and φ are the co-ordinates of the point P and c is the velocity of light. These two vectors are mutually perpendicular to each other, so that we have for the Poynting vector at P

$$S = \frac{c}{4\pi}\left[EH\right] = \frac{c \cdot e^2 \sin^2\theta \cdot f^2}{4\pi c^4 r^2} \quad \ldots \quad \ldots \quad (1)$$

The energy radiated between the cones having semi-angles θ and $\theta + d\theta$ will be obtained by multiplying the above with the solid angle $2\pi r^2 \sin\theta \, d\theta$. The total energy radiated in all directions is then obtained by integrating the result between the limits $\theta = 0$ and $\theta = \pi$ as

$$\frac{2\pi r^2 . e^2 f^2}{4\pi c^3 r^2} \int_0^\pi \sin^3\theta \, d\theta = \frac{2e^2 f^2}{3c^3}. \qquad .. \qquad .. \quad (2)$$

Radiation from an Oscillating Dipole.—If the charge e, situated at the centre of the sphere, is oscillating in such a manner that the displacement at any instant of time t is given by $E_0 \cos 2\pi\nu t$, the Poynting vector S at a point θ, φ of the surface will be given by

$$\frac{c}{4\pi} . \frac{e^2 \sin^2\theta}{c^4 r^2} . E_0^2 (2\pi\nu)^4 \cos^2 2\pi\nu t.$$

This is identical with (1) except that the acceleration f has been replaced by $-E_0 (2\pi\nu)^2 \cos 2\pi\nu t$. We are justified in doing this, only if the amplitude E_0 of the oscillation is quite small in comparison with r. Only then will the charge remain approximately at the origin of the sphere at all instants. The mean rate of radiation in the direction θ is therefore given by

$$\frac{(2\pi\nu)^4 . e^2 E_0^2 \sin^2\theta}{8\pi c^3 r^2} \ldots \qquad .. \qquad .. \quad (3)$$

On multiplying (3) with the solid angle $2\pi r^2 \sin\theta \, d\theta$ and integrating over the surface of a sphere of radius r as before, we obtain the expression for the total radiation as

$$\frac{\omega^4 e^2 E_0^2}{3c^3}. \qquad .. \qquad .. \qquad .. \quad (4)$$

eE_0 represents the maximum value of the moment that would be acquired by the oscillating dipole and ω stands for $2\pi\nu$.

APPENDIX II

CONVERGENCE CORRECTION

In the general case of a rectangular co-ordinate system OXYZ, we have shown (equations 21, 22 and 23 of chapter III) that if E_x, E_y and E_z are the X, Y and Z components respectively of an incident electric vector, then the averages of the squares of the optic moments induced in the molecules in the directions X, Y and Z are

$$\overline{p_z^2} = E_z^2H^2+(E_x^2+E_y^2)k^2$$
$$\overline{p_y^2} = E_y^2H^2+(E_z^2+E_x^2)k^2$$
$$\overline{p_x^2} = E_x^2H^2+(E_y^2+E_z^2)k^2$$

where $H^2 = \frac{1}{5}(A^2+B^2+C^2)+\frac{2}{15}(AB+BC+AC)$,

$$k^2 = \tfrac{1}{15}(A^2+B^2+C^2-AB-BC-AC). \quad .. \quad (1)$$

If we regard that the direction of propagation of the incident unpolarized light is confined strictly to the OY axis, then $E_z = E_x = E$ and $E_y = 0$. The depolarization ϱ of the scattered light, obtained under such ideal conditions, will be

$$\varrho = \frac{\overline{p_y^2}}{\overline{p_z^2}} = \frac{2k^2}{H^2+k^2}.$$

On the other hand, if we consider a ray OM (Fig. ii) whose

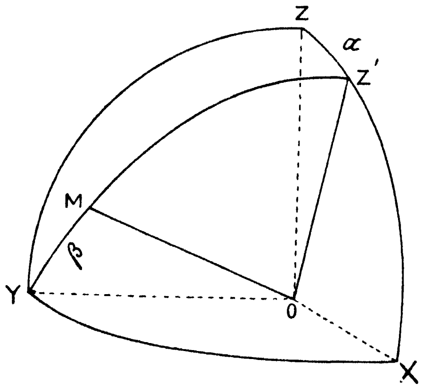


FIG. ii.

direction of propagation departs from the OY axis in that it lies in the YOZ′ plane such that $Y\hat{O}M = \beta$ and $Z\hat{O}Z' = \alpha$, then the electric vector E lying in the plane YOZ′ will be normal to the direction of propagation OM. It will have components $-E\sin\beta$ along OY and $E\cos\beta$ along OZ′ which in its turn may be resolved into $E\cos\beta\cos\alpha$ along OZ and $E\cos\beta\sin\alpha$ along OX. The intensity E, lying in a direction perpendicular to OM and to the plane YOZ′, will have no component along OY but will give rise to $-E\sin\alpha$ along OZ and $E\cos\alpha$ along OX. We therefore have

$$E_z = E(\cos\beta\cos\alpha - \sin\alpha); \quad E_y = -E\sin\beta; \quad E_x = E(\cos\beta\sin\alpha + \cos\alpha).$$

Substituting these in equations (1), we have

$$\overline{p_z^2} = E^2H^2(\cos^2\beta\cos^2\alpha + \sin^2\alpha - 2\sin\alpha\cos\alpha\cos\beta) + E^2k^2(1 + \cos^2\alpha\sin^2\beta + 2\cos\beta\sin\alpha\cos\alpha),$$

$$\overline{p_y^2} = E^2H^2\sin^2\beta + E^2k^2(1 + \cos^2\beta).$$

If a lens is used to condense the beam symmetrically round the axis OY, its semi-angle of convergence being Ω, we can easily see that in the above equations, β varies from 0 to Ω and α from 0 to 2π. The average values of these expressions, which represent the intensities, must therefore be obtained. It may be noted that in doing so, we are merely adding up the intensities arising from rays of different obliquities as if they are all optically incoherent. Denoting these averages by $\overline{\overline{p_z^2}}$ and $\overline{\overline{p_y^2}}$, they may be evaluated in the usual way as

$$\overline{\overline{p_z^2}} = E^2H^2\left\{\tfrac{1}{6}(4 + \cos\Omega + \cos^2\Omega)\right\} + E^2k^2\left\{\tfrac{1}{6}(8 - \cos\Omega - \cos^2\Omega)\right\}$$

$$\overline{\overline{p_y^2}} = E^2H^2\left\{\tfrac{1}{3}(2 - \cos\Omega - \cos^2\Omega)\right\} + E^2k^2\left\{\tfrac{1}{3}(4 + \cos\Omega + \cos^2\Omega)\right\}.$$

The depolarization will now be given as

$$\varrho' = \frac{\overline{\overline{p_y^2}}}{\overline{\overline{p_z^2}}} = \frac{2k^2 + (H^2 - k^2)\psi}{H^2 + k^2 - \tfrac{1}{2}(H^2 - k^2)\psi} \quad \text{where } \psi = \tfrac{1}{3}(2 - \cos\Omega - \cos^2\Omega).$$

It may easily be verified that if Ω, the semi-angle of convergence equals zero, then the function ψ reduces to zero and ϱ' reduces to $\dfrac{2k^2}{H^2 + k^2}$ which is the value in an ideal

case. Dividing throughout by H^2+k^2, the above relation may be written as

$$\varrho' = \frac{\varrho+(1-\varrho)\psi}{1-\left(\frac{1-\varrho}{2}\right)\psi}.$$

This expression may be further simplified if we regard ϱ and Ω as small. Under such conditions, neglecting higher powers of Ω, we may write ψ as equal to $2\sin^2\frac{\Omega}{2}$ and neglecting higher powers of ϱ, we have

$$\varrho' = \varrho+(2-\varrho)\sin^2\frac{\Omega}{2} \doteq \varrho+\frac{\Omega^2}{2}. \qquad \text{.. (2)}$$

APPENDIX III

FLUCTUATIONS[1]

Gaussian Error Function.—If x denotes any physical quantity characteristic of a medium, the probability, that this may, when referred to a small volume element within the medium, have a value differing from the mean value x_0 by an amount lying between y and $y+dy$, is given by the Gaussian error function (1).

$$\omega = \left(\frac{\lambda}{2\pi}\right)^{\frac{1}{2}} e^{-\frac{1}{2}\lambda y^2} dy, \quad \ldots \quad \ldots \quad (1)$$

where $\lambda = \frac{1}{\overline{y^2}}$.

$\overline{y^2}$ is the same as $\overline{(\triangle x)^2}$ and is a measure of the fluctuation of x. Conversely, if we can express the probability function in respect of a particular physical quantity in the form of (1), we may easily evaluate the fluctuation of that physical quantity.

Fluctuations of Volume, Temperature and Number.—If W represents the work that has to be done in transforming a volume element from the mean value state to any other through a reversible process, the probability that the volume element may spontaneously reside in the latter state is proportional to $e^{-W/kT}$. This fact is represented by (2).

$$\omega \propto e^{-W/kT} \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

If, as a result of the transformation, the energy of the volume element increases by $\triangle E$, its entropy by $-\triangle S$ and volume by $\triangle V$, we have

$$W = \triangle E - T\triangle S + p\triangle V \quad \ldots \quad \ldots \quad (3)$$

T and p are the temperature and pressure respectively of the medium and therefore also represent the mean values when

[1] Evaluation of the fluctuations of volume, temperature, number, pressure and entropy closely follows that given by Landau and Lifshitz in their book on *Statistical Physics* (1938). The derivation in the case of binary mixtures is taken from Raman and Ramanathan, Phil. Mag., *45*, 213 (1923).

referred to the volume element. If we regard the energy E as a function of entropy S and volume V, we may write $\triangle E$ as follows, after neglecting higher powers.

$$\triangle E = \frac{\partial E}{\partial S}\triangle S+\frac{\partial E}{\partial V}\triangle V+ \frac{1}{2}\left[\frac{\partial^2 E}{\partial S^2}(\triangle S)^2+2\frac{\partial^2 E}{\partial S\partial V}\triangle S\triangle V+\frac{\partial^2 E}{\partial V^2}(\triangle V)^2\right]. \quad (4)$$

Making use of the relations $T = \left(\frac{\partial E}{\partial S}\right)_V$ and $p = -\left(\frac{\partial E}{\partial V}\right)_S$ and combining (4) with (3), we obtain (5).

$$\begin{aligned} W &= \frac{1}{2}\left[\frac{\partial^2 E}{\partial S^2}(\triangle S)^2+2\frac{\partial^2 E}{\partial S\partial V}\triangle S\triangle V+\frac{\partial^2 E}{\partial V^2}(\triangle V)^2\right] \\ &= \frac{1}{2}\left[\triangle S\triangle\left(\frac{\partial E}{\partial S}\right)_V+\triangle V\triangle\left(\frac{\partial E}{\partial V}\right)_S\right] \\ &= \tfrac{1}{2}(\triangle S\triangle T-\triangle p\triangle V). \quad (5) \end{aligned}$$

(2) will now be written as

$$\omega \propto e^{(\triangle p\triangle V-\triangle S\triangle T)/2kT} \quad (6)$$

p, V, S and T are involved in (6) and any two of these quantities may be chosen as the independent variables. If V and T are chosen as the independent variables, we have

$$\left.\begin{aligned} \triangle S &= \left(\frac{\partial S}{\partial T}\right)_V\triangle T+\left(\frac{\partial S}{\partial V}\right)_T\triangle V = \frac{c_v}{T}\triangle T+\left(\frac{\partial p}{\partial T}\right)_V\triangle V \\ \triangle p &= \left(\frac{\partial p}{\partial T}\right)_V\triangle T+\left(\frac{\partial p}{\partial V}\right)_T\triangle V \end{aligned}\right\}. \quad (7)$$

Substituting (7) in (6) and rewriting it as a product of two functions, we get (8).

$$\omega \propto e^{\frac{(\triangle V)^2}{2kT}\left(\frac{\partial p}{\partial V}\right)_T} . e^{-\frac{c_v}{2kT^2}(\triangle T)^2} \quad (8)$$

The first of these functions contains $\triangle V$ only and the second $\triangle T$ only. By applying the theorem of multiplication of probabilities, we may conclude that the fluctuations of V and T take place independently of each other. Each of the above functions is of the form of (1). By comparing them in turn with (1), we get the following relations.

$$\overline{\Delta V \Delta T} = 0$$

$$\overline{(\Delta V)^2} = -kT\left(\frac{\partial V}{\partial p}\right)_T$$

$$\overline{(\Delta T)^2} = \frac{kT^2}{c_v}. \quad \ldots \quad \ldots \quad \ldots \quad (9)$$

If ν represents the mean number of molecules per c.c., the volume element V will have a total number equal to $V\nu$ which is a constant. We therefore have

$$\frac{\overline{(\Delta V)^2}}{V^2} = \frac{\overline{(\Delta \nu)^2}}{\nu^2}$$

Substituting in (9), we obtain (10) for the fluctuation of number.

$$\overline{(\Delta \nu)^2} = \frac{-kT\nu^2}{V^2}\left(\frac{\partial V}{\partial p}\right)_T = \frac{RT\beta\nu^2}{NV}. \quad \ldots \quad (10)$$

Fluctuations of Pressure and Entropy.—If p and S are chosen as the independent variables, we have

$$\left.\begin{aligned} \Delta V &= \left(\frac{\partial V}{\partial p}\right)_S \Delta p + \left(\frac{\partial V}{\partial S}\right)_p \Delta S = \left(\frac{\partial V}{\partial p}\right)_S \Delta p + \left(\frac{\partial T}{\partial p}\right)_S \Delta S \\ \Delta T &= \left(\frac{\partial T}{\partial S}\right)_p \Delta S + \left(\frac{\partial T}{\partial p}\right)_S \Delta p = \frac{T}{c_p}\Delta S + \left(\frac{\partial T}{\partial p}\right)_S \Delta p \end{aligned}\right\}. \quad (11)$$

Substituting (11) in (6) and rewriting it as a product of two functions, we get (12).

$$\omega \propto e^{\frac{(\Delta p)^2}{2kT}\left(\frac{\partial V}{\partial p}\right)_S} \cdot e^{-\frac{(\Delta S)^2}{2kc_p}} \quad . \quad \ldots \quad \ldots \quad (12)$$

Proceeding as before, we obtain relations (13).

$$\overline{\Delta p \Delta S} = 0$$

$$\overline{(\Delta p)^2} = -kT\left(\frac{\partial p}{\partial V}\right)_S$$

$$\overline{(\Delta S)^2} = kc_p. \quad \ldots \quad \ldots \quad \ldots \quad (13)$$

Fluctuations of Concentration and Pressure in a Binary Mixture.—Let us consider a volume element V of the mixture. Let m_1 and m_2 represent the masses of the two components present per unit volume when the volume element is in equilibrium with the rest of the medium. The mean concentration

$\frac{m_2}{m_1}$ of the mixture will be denoted by c. If an amount of work W has to be done in order that the volume element may be transformed, by a reversible process, into another state characterized by a concentration $c+\triangle c$, we have

$$\omega \propto e^{-W/kT}, \quad .. \quad .. \quad .. \quad (14)$$

where ω is the probability of the new state. We must now evaluate W and recast (14) in the form of (1) in order to obtain the fluctuations of the various physical quantities. W may be expressed as a function of any two independent variables but we shall now choose the concentration c and the pressure p of the volume element as the variables.

We shall imagine a cylinder fitted with a frictionless piston and containing a unit volume of the mixture at concentration c and a hydrostatic pressure equal to the vapour pressure of the mixture. The base of the cylinder has two openings, which may be either closed at will or fitted with membranes permeable respectively to the vapour of the first and second component only. A second and much larger cylinder of the same type as above, which serves as a reservoir, is assumed to be filled with a large quantity of the liquid mixture. The temperature of the latter is the same as that of the former and its hydrostatic pressure is again equal to the total vapour pressure φ of the mixture. These conditions are the same as those that will prevail when the volume element, which corresponds to the small cylinder in this case, is in equilibrium with the rest of the medium (reservoir in this case). The following isothermal reversible operations may then be carried out. By means of auxiliary pumps, small masses $\triangle m_1$ and $\triangle m_2$ of the two components may be removed in the state of vapour from the reservoir through the semi-permeable membranes. The volume of the reservoir is so great that any alteration in the composition of its contents that occurs may be considered negligible. If p_1 and p_2 be respectively the partial pressure of the vapours and v_1 and v_2 their specific volumes, the work done in this process is

$$-p_1v_1\triangle m_1-p_2v_2\triangle m_2+[s_1\triangle m_1+s_2\triangle m_2]\varphi, \quad .. \quad (A)$$

where s_1 and s_2 represent respectively the shrinkages of the volume

of the mixture by removal of unit masses of the two components. From the vapours thus separated, a mass $\triangle m_1$ of the first component and a mass $c\triangle m_1$ of the second component are forced simultaneously into the small cylinder. It is clear that in this operation, the composition of the mixture in the small cylinder and therefore also its vapour pressure, remain unaltered. The work done in this process is

$$p_1 v_1 \triangle m_1 + p_2 v_2 c \triangle m_1 - [s_1 \triangle m_1 + s_2 c \triangle m_1]\varphi \quad .. \quad \text{(B)}$$

The remaining portion, $\triangle m_2 - c\triangle m_1$, of the second component is now forced into the cylinder, the hydrostatic pressure in it being maintained at the quilibrium value of its total vapour pressure at each instant. The work done in this process is

$$v_2(\triangle m_2 - c\triangle m_1)(p_2 + \tfrac{1}{2}\triangle p_2) - s_2(\triangle m_2 - c\triangle m_1)(\varphi + \tfrac{1}{2}\triangle\varphi) \,. \quad \text{(C)}$$

$\triangle p_2$ and $\triangle\varphi$ represent respectively the changes of the partial vapour pressure and the total vapour pressure resulting from the operation. The volume of the mixture in the smaller cylinder is now greater than at first by $s_1\triangle m_1 + s_2\triangle m_2$. The semi-permeable openings are now closed and the piston forced in, thus increasing the hydrostatic pressure, till the original volume is restored. The work done in this process is

$$\tfrac{1}{2}\beta(\triangle p)^2 \,. \quad .. \quad .. \quad .. \quad \text{(D)}$$

β is the isothermal compressibility of the mixture and $\triangle p$ is the increase of hydrostatic pressure in the last process. As a result of the operations A, B, C and D, the concentration of the mixture in the small cylinder is evidently altered from c to $c+\triangle c$ such that $m_1\triangle c = \triangle m_2 - c\triangle m_1$. The total work done is obtained as follows by adding A, B, C and D.

$$\tfrac{1}{2}(v_2\triangle p_2 - s_2\triangle\varphi)(\triangle m_2 - c\triangle m_1) + \tfrac{1}{2}\beta(\triangle p)^2 \,. \quad .. \quad (15)$$

(15) may be written in the form of (16).

$$\tfrac{1}{2}m_1\left(v_2\frac{\partial p_2}{\partial c} - s_2\frac{\partial\varphi}{\partial c}\right)(\triangle c)^2 + \tfrac{1}{2}\beta(\triangle p)^2 \,. \quad .. \quad (16)$$

(16) represents the work done per unit volume. Accordingly we have

$$W = \tfrac{1}{2}Vm_1\left(v_2\frac{\partial p_2}{\partial c} - s_2\frac{\partial\varphi}{\partial c}\right)(\triangle c)^2 + \tfrac{1}{2}V\beta(\triangle p)^2 \,. \quad (17)$$

Substituting (17) in (14) and expressing it as before as the product of two terms, we see that the fluctuations of concentration and pressure take place independently of each other and we get the following relations.

$$\overline{\triangle c \triangle p} = 0$$

$$\overline{(\triangle c)^2} = \frac{kT}{Vm_1\left(v_2 \frac{\partial p_2}{\partial c} - s_2 \frac{\partial \varphi}{\partial c}\right)}$$

$$\overline{(\triangle p)^2} = \frac{kT}{\beta V} \cdot \quad .. \quad .. \quad .. \quad .. \quad (18)$$

The value of $\overline{(\triangle p)^2}$ is the same as that given in (13). If ε stands for the dielectric constant of the medium, by regarding it as a function of c and p, we obtain

$$\triangle \varepsilon = \frac{\partial \varepsilon}{\partial c} \cdot \triangle c + \frac{\partial \varepsilon}{\partial p} \cdot \triangle p \cdot$$

From (18), we at once get an expression for the fluctuation of ε in respect of the volume element V.

$$\overline{(\triangle \varepsilon)^2} = \frac{kT}{V}\left[\left(\frac{\partial \varepsilon}{\partial c}\right)^2 \Big/ m_1\left(v_2 \frac{\partial p_2}{\partial c} - s_2 \frac{\partial \varphi}{\partial c}\right) + \left(\frac{\partial \varepsilon}{\partial p}\right)^2 \cdot \frac{1}{\beta}\right] \cdot \quad .. \quad (19)$$

If $\frac{\partial \varepsilon}{\partial p}$ is rewritten as $\frac{\partial \varepsilon}{\partial \sigma} \cdot \frac{\partial \sigma}{\partial p}$ where σ is the density of the medium, remembering that $\frac{1}{\sigma} \cdot \frac{\partial \sigma}{\partial p}$ is also equal to β, we get (20) in the place of (19).

$$\overline{(\triangle \varepsilon)^2} = \frac{RT}{NV}\left[\left(\frac{\partial \varepsilon}{\partial c}\right)^2 \Big/ m_1\left(v_2 \frac{\partial p_2}{\partial c} - s_2 \frac{\partial \varphi}{\partial c}\right) + \sigma^2 \beta \left(\frac{\partial \varepsilon}{\partial \sigma}\right)^2\right] \cdot \quad .. \quad (20)$$

Appendix IV

EVALUATION OF THE VARIOUS MATRIX ELEMENTS OF THE POLARIZABILITY TENSOR

The intensity of a Raman line $v \rightarrow v'$ depends upon the matrix element $\alpha_{vv'}$ and this is given by (1).

$$\alpha_{vv'} = \int \psi^*_{v'}(q)\, \alpha(q)\, \psi_v(q)\, dq \,. \qquad .. \qquad .. \quad (1)$$

We may expand $\alpha(q)$ in the form

$$\alpha(q) = \alpha_0 + \sum_j \left(\frac{\partial \alpha}{\partial q_j}\right)_0 q_j + \frac{1}{2} \sum_{jk} \left(\frac{\partial^2 \alpha}{\partial q_j \partial q_k}\right)_0 q_j q_k + \ldots \qquad .. \quad (2)$$

and substitute this series in (1). The explicit value of $\alpha_{vv'}$ is then obtained as the sum of a number of integrals, the exact values of which will depend upon the transition $v \rightarrow v'$. In some cases, integrals involving odd powers of q and in others, those involving even powers of q vanish. The exact values for various cases have been given in the text. One example will be worked out here in detail and all others may easily be derived by adopting similar methods.

We shall select the transition $v \rightarrow v+2$ and evaluate $\alpha_{v,\, v+2}$. It may easily be shown that the integrals arising from the first term and all other terms involving odd powers of q in the series (2) vanish. The most important term in this series will therefore be

$$\frac{1}{2}\left(\frac{\partial^2 \alpha}{\partial q^2}\right)_0 \int \psi^*_{v+2}(q)\, q^2\, \psi_v(q)\, dq \,. \qquad .. \qquad .. \quad (3)$$

$\psi_v(q)$ is the eigen function of a harmonic oscillator and is given by

$$\frac{1}{\sqrt{a}} \sqrt{\frac{1}{2^v \underline{|v} \pi^{\frac{1}{2}}}}\; e^{-\frac{1}{2}\left(\frac{q}{a}\right)^2} . \mathrm{H}_v \left(\frac{q}{a}\right),$$

where $a^2 = 2c$ and c stands for $h/8\pi^2 \nu \mu$. H_v is the Hermite polynomial of degree v. Substituting the values of the eigen functions in (3) and changing the variable dq to $d\left(\frac{q}{a}\right)$, we have

$$\alpha_{v,v+2} = \frac{1}{2}\left(\frac{\partial^2\alpha}{\partial q^2}\right)_0 \sqrt{\frac{1}{2^{v+2}\underline{|v+2}\pi^{\frac{1}{2}}2^v\underline{|v}\pi^{\frac{1}{2}}}} \int e^{-\left(\frac{q}{a}\right)^2} q^2 H_{v+2}\left(\frac{q}{a}\right) H_v\left(\frac{q}{a}\right) d\left(\frac{q}{a}\right). \quad .. \quad (4)$$

We can now express $q^2 H_v\left(\frac{q}{a}\right)$ as follows.

$$q^2 H_v\left(\frac{q}{a}\right) = a^2\left[A_{v+2}H_{v+2}\left(\frac{q}{a}\right) + A_v H_v\left(\frac{q}{a}\right) \ldots\right]. \quad .. \quad (5)$$

If (5) is substituted in (4), it is easily seen that all the terms, except the one which has A_{v+2} for its coefficient, contribute nothing to the integral. This result follows from the orthogonal properties of the polynomial expressed in (6).

$$\int e^{-\left(\frac{q}{a}\right)^2} H_m\left(\frac{q}{a}\right) H_n\left(\frac{q}{a}\right) d\left(\frac{q}{a}\right) = \begin{cases} 0 \ldots\ldots\ldots m \neq n \\ 2^v\underline{|v}\pi^{\frac{1}{2}} \ldots\ldots m = n = v. \end{cases} \quad .. \quad (6)$$

By equating the coefficients of the term of order $v+2$ on both sides of (5), we see that $A_{v+2} = \frac{1}{4}$ since the coefficient of the term of order v in H_v is 2^v.

Therefore

$$\alpha_{v,v+2} = \frac{a^2}{8}\left(\frac{\partial^2\alpha}{\partial q^2}\right)_0 \sqrt{\frac{1}{2^{v+2}\underline{|v+2}\,\pi^{\frac{1}{2}}2^v\,\underline{|v}\,\pi^{\frac{1}{2}}}} \times$$

$$\int e^{-\left(\frac{q}{a}\right)^2} H_{v+2}\left(\frac{q}{a}\right) H_{v+2}\left(\frac{q}{a}\right) d\left(\frac{q}{a}\right). \quad .. \quad (7)$$

Substituting from (6) in (7) and simplifying, we have

$$\alpha_{v,v+2} = \frac{1}{2}\left(\frac{\partial^2\alpha}{\partial q^2}\right)_0 c\sqrt{(v+1)(v+2)}\cdot$$

In this manner, all the integrals occurring in chapter XI of the text may be evaluated. In each case, one of the Hermite polynomials under the integral has to be expressed as the sum of a series of such polynomials and use has to be made of their well-known orthogonal properties.

As an example of the integrals occurring under the subject of rotational Raman effect, we shall select the one relating to the Z component of a transition $Jm \rightarrow J'm'$. The corresponding intensity will be proportional to

$$\left|(\alpha_{00})^{Jm}_{J'm'}\right|^2$$

Since $\lambda+\mu=0$, owing to the selection rule $m'-m=\lambda+\mu$, we need consider cases in which $m'=m$ only. As has been explained in the text, we have

$$(\alpha_{0\,0})^{Jm}_{J'm'} = \delta^{m'-m}_{\lambda'+\mu'} \int \sum_{\lambda'\mu'} (\alpha'_{\lambda\mu}) D_{\lambda-\lambda'} D_{\mu-\mu'} \overset{*}{\Theta}_{J'm} \Theta_{Jm} \sin\theta \, d\theta.$$

The dashed terms refer to the axes fixed in the molecule. For the case under consideration ($\lambda+\mu=0$), the only terms that survive in the summation under the integral are those involving $\alpha_0{}'_0$, $\alpha_1{}'_{-1}$ and $\alpha_{-1}{}'_1$. Since we are dealing with diatomic or linear molecules only, we may put $\alpha'_{1\,-1}=\alpha'_{-1\,1}$. Substituting the values of $D_{\lambda-\lambda'}$, etc., and denoting the normalizing factors by the N's, we have

$$(\alpha_{0\,0})^{Jm}_{J'm} = N_{Jm} N_{J'm} \int \left[\alpha_0 + (\cos^2\theta - \tfrac{1}{3})(\alpha'_{00} - \alpha'_{1\,-1}) \right] \overset{*}{P}_{J'm} P_{Jm} \sin\theta \, d\theta. \quad \text{.. (8)}$$

We shall now use the following relation, derived from the known properties of the associated Legendre functions.

$$\cos^2\theta \,.\, P_{Jm} = \frac{(J+m)(J+m-1)}{(2J+1)(2J-1)} P_{J-2,\,m} + \left[\frac{(J-m)(J+m)}{(2J-1)(2J+1)} + \frac{(J-m+1)(J+m+1)}{(2J+1)(2J+3)} \right] P_{Jm} + \frac{(J-m+2)(J-m+1)}{(2J+1)(2J+3)} P_{J+2,\,m}. \quad \text{.. (9)}$$

On substituting (9) in (8), we at once see that the selection rule for J in this case is $J'=J$ or $J \pm 2$. Squaring the right hand side and summing up each term for all possible values of m, namely $m=0, \pm 1 \ldots\ldots \pm J$, we get the following relations.

$$\frac{1}{2J+1} \left| (\alpha_{0\,0})^{Jm}_{J-2,\,m} \right|^2 = \frac{2}{15} \frac{J(J-1)}{(2J+1)(2J-1)} \left| (\gamma_0) \right|^2$$

$$\frac{1}{2J+1} \left| (\alpha_{0\,0})^{Jm}_{Jm} \right|^2 = \left| (\alpha_0) \right|^2 + \frac{4}{45} \frac{J(J+1)}{(2J-1)(2J+3)} \left| (\gamma_0) \right|^2$$

$$\frac{1}{2J+1} \left| (\alpha_{0\,0})^{Jm}_{J+2,\,m} \right|^2 = \frac{2}{15} \frac{(J+1)(J+2)}{(2J+1)(2J+3)} \left| (\gamma_0) \right|^2$$

$$3\alpha_0 = \alpha_0{}'_0 + \alpha_1{}'_{-1} + \alpha_{-1}{}'_1 \quad ; \quad \gamma_0 = \alpha_0{}'_0 - \alpha_1{}'_{-1}.$$

These have been given in the text. Other integrals may be dealt with in a similar manner.

Appendix V

TENSOR COMPONENTS AND THEIR TRANSFORMATION FROM ONE CO-ORDINATE SYSTEM TO ANOTHER

In a system of cartesian co-ordinates x, y, z, if the components of two vectors are related by the equations (1),

$$
\begin{aligned}
p_x &= \alpha_{xx}u_x + \alpha_{xy}u_y + \alpha_{xz}u_z \\
p_y &= \alpha_{yx}u_x + \alpha_{yy}u_y + \alpha_{yz}u_z \\
p_z &= \alpha_{zx}u_x + \alpha_{zy}u_y + \alpha_{zz}u_z, \qquad \ldots \qquad \ldots \qquad (1)
\end{aligned}
$$

α is a tensor and its components are transformed by a change of co-ordinates in accordance with the well-known set of equations (2).

$$\alpha_{xy} = \sum_{x'y'} \alpha'_{xy} \cos xx' \cos yy'. \qquad \ldots \qquad \ldots \qquad (2)$$

In particular, when u and p represent the same vector referred to two sets of rectangular co-ordinates, the tensor components will merely be the direction cosines of one set of axes in respect of the other and we have (3).

$$
\begin{aligned}
p_x &= p_x' \cos xx' + p_y' \cos xy' + p_z' \cos xz' \\
p_y &= p_x' \cos yx' + p_y' \cos yy' + p_z' \cos yz' \\
p_z &= p_x' \cos zx' + p_y' \cos zy' + p_z' \cos zz'. \qquad \ldots \qquad (3)
\end{aligned}
$$

If we are dealing with circular co-ordinates $\frac{1}{\sqrt{2}}(x+iy)$, $\frac{1}{\sqrt{2}}(x-iy)$ and z introduced in chapter XI, we have (1a), (2a) and (3a) in the place of the transformations (1), (2) and (3). We shall represent these co-ordinates by the letters λ, μ, etc., and designate them by the suffixes 1, -1 and 0 respectively.

$$
\begin{aligned}
p_1 &= \alpha_{1\,-1}u_1 + \alpha_{1\,1}u_{-1} + \alpha_{1\,0}u_0 \\
p_{-1} &= \alpha_{-1\,-1}u_1 + \alpha_{-1\,1}u_{-1} + \alpha_{-1\,0}u_0 \\
p_0 &= \alpha_{0\,-1}u_1 + \alpha_{0\,1}u_{-1} + \alpha_{0\,0}u_0. \qquad \ldots \qquad \ldots \qquad (1a)
\end{aligned}
$$

$$\alpha_{\lambda\mu} = \sum_{\lambda'\mu'} \alpha'_{\lambda\mu} D_{\lambda-\lambda'} D_{\mu-\mu'}. \qquad \ldots \qquad \ldots \qquad \ldots \qquad (2a)$$

$$p_1 = p_1'D_{1\,-1}+p_{-1}'D_{1\,1}+p_0'D_{1\,0}$$
$$p_{-1} = p_1'D_{-1\,-1}+p_{-1}'D_{-1\,1}+p_0'D_{-1\,0}$$
$$p_0 = p_1'D_{0\,-1}+p_{-1}'D_{0\,1}+p_0'D_{0\,0}. \qquad .. \quad (3a)$$

By substituting the appropriate values of p_1, u_1, etc., namely $\frac{1}{\sqrt{2}}(p_x+ip_y)$, $\frac{1}{\sqrt{2}}(p_x'+ip_y')$, etc., respectively in (1*a*) or for p_1 and p_1' in (3*a*) and by comparing the expressions with the analogous ones for cartesian co-ordinates, we can easily express the D's and the α's in the circular co-ordinate system in terms of their values in the cartesian co-ordinate system and verify the transformations given under the section on rotational Raman scattering in chapter XI. In the cartesian co-ordinates α_{xx}, α_{yy} and α_{zz} are the diagonal components of the tensor and $\alpha_{xx}+\alpha_{yy}+\alpha_{zz}$ is an invariant of the tensor. In the circular co-ordinates, $\alpha_{1\,-1}$, $\alpha_{-1\,1}$ and $\alpha_{0\,0}$ are the diagonal components of the tensor and $\alpha_{1\,-1}+\alpha_{-1\,1}+\alpha_{0\,0}$ is the corresponding invariant.

APPENDIX VI

GROUPS AND GROUP CHARACTERS

Definition of a Group.—Any set of elements a, b, c, ... , finite or infinite in number, is said to form a group under an operation R, if the elements satisfy the following postulates.

(i) The set is closed under the operation R, i.e., for every two elements a, b in the set, $a\mathrm{R}b$ is also an element in the set.

(ii) For any three elements a, b, c, the associative law $(a\mathrm{R}b)\mathrm{R}c = a\mathrm{R}(b\mathrm{R}c)$ is true.

(iii) There exists in the set an element E called the identity with the property $a\mathrm{RE} = \mathrm{ER}a = a$ for every element a in the set.

(iv) To every element a in the set, there exists another element called the inverse element of a and written as a^{-1} such that $a\mathrm{R}a^{-1}=\mathrm{E}$.

The total number of elements which may be denoted by N is called the order of the group. The complete set of symmetry operations characteristic of either a crystal lattice or a molecule furnish a typical illustration of a group.

Groups of Linear Homogeneous Substitutions and Representation of an Abstract Group.—Let $(x_1, x_2 \ldots x_n)$ represent a set of n independent co-ordinates. A linear homogeneous substitution of order n arises from n equations of the form

$$\begin{aligned} x_1' &= a_{1\,1}x_1 + a_{1\,2}x_2 \ldots\ldots\ldots\ldots + a_{1\,n}x_n \\ x_2' &= a_{2\,1}x_1 + a_{2\,2}x_2 \ldots\ldots\ldots\ldots + a_{2\,n}x_n \\ &\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ x_n' &= a_{n\,1}x_1 + a_{n\,2}x_2 \ldots\ldots\ldots\ldots + a_{n\,n}x_n . \end{aligned}$$

It is uniquely determined by the matrix of transformation

$$\begin{vmatrix} a_{1\,1} & a_{1\,2} & \ldots & \ldots & \ldots & \ldots & a_{1\,n} \\ a_{2\,1} & a_{2\,2} & \ldots & \ldots & \ldots & \ldots & a_{2\,n} \\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\ a_{n\,1} & a_{n\,2} & \ldots & \ldots & \ldots & \ldots & a_{n\,n} \end{vmatrix} .$$

A group H of linear substitutions is a group of matrices determined by these linear substitutions. If G is any abstract group

and H is a group of linear substitutions and if to every element A of G, there corresponds an element A′ of H, such that the product of two elements A and B of G corresponds to the product of the two corresponding elements A′, B′ of H, then the group of matrices H is called a representation of G.

Equivalent Representations and Group Characters.—Let E, A, B, C,—be a set of matrices forming a group H and S be any fixed matrix. Now take the matrices E, $S^{-1}A\,S$, $S^{-1}B\,S$,—. It may easily be shown that these matrices also form a group and it can be conveniently represented by $S^{-1}H\,S$. Now if H is a representation of an abstract group G, obviously $S^{-1}H\,S$ is also a representation of the group G. Two such representations are called equivalent.

If the matrix $A = (a_{ik})$, the determinantal equation

$$\begin{vmatrix} a_{11}-t & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22}-t & \cdots & a_{2n} \\ \cdot\cdot & \cdot\cdot & \cdots & \cdot\cdot \\ a_{n1} & a_{n2} & \cdots & a_{nn}-t \end{vmatrix} = 0$$

is called the character equation of A and $\Sigma\, a_{ii} = \chi\,(A)$ is called the character of A. It is easy to see that the character equation of A is the same as the character equation of $S^{-1}A\,S$. *Hence the character of an element is the same in equivalent representations.*

Reducible and Irreducible Substitution Groups.—A group of homogeneous linear substitutions is spoken of as *reducible*, if it is possible to find a set of linear functions of the variables $(x_1, x_2 \ldots\ldots\ldots x_n)$ less in number than the variables such that they are transformed among themselves by every operation of the group. If it is not possible to find such a set of linear functions of the variables, the group of substitutions is said to be *irreducible*. A reducible group of homogeneous linear substitutions is called completely reducible when it is possible to choose the variables in such a way that (i) they fall into sets, each set of variables being transformed among themselves by every operation of the group while, (ii) the group in each set is irreducible.

APPENDIX VII

GROUP THEORY AND NORMAL OSCILLATIONS OF MOLECULES

Normal Modes and Irreducible Representations.—Let there be n atoms in a molecule. The position of the atoms may be described by specifying the $3n$ cartesian co-ordinates x_1, y_1, z_1 $\ldots . x_n$, y_n, z_n. These may be taken to correspond to zero values for the equilibrium position. For oscillations of small amplitudes, the potential and kinetic energies may be expressed as general quadratic functions of the co-ordinates. These may be simultaneously reduced to the canonical form

$$2V = \Sigma \lambda_i Q_i^2 ; \quad 2T = \Sigma \dot{Q}_i^2$$

with the help of suitable linear transformation of co-ordinates. Q_1, Q_2, $\ldots . . Q_{3n}$ are called the normal co-ordinates and the corresponding normal frequencies are given by the equations $4\pi^2\nu_k^2 = \lambda_k$. The normal co-ordinate Q_k defines a configuration of the molecule. If we perform a symmetry operation R on the molecule, we get a new configuration which we denote by RQ_k. If by means of the operation R, the kth atom goes over into the lth atom, we shall suppose that the lth atom remains in its own neighbourhood but gets the motion of the kth atom. By doing this for every atom, we keep all the atoms in the neighbourhood of their original equilibrium positions and obtain a configuration of the molecule which is geometrically identical with RQ_k. If we denote this new configuration by RQ_k, RQ_k evidently represents a normal co-ordinate having the same frequency ν_k because the relative configuration of the atoms is not altered. If RQ_k is distinct from Q_k, we obtain two distinct modes of oscillation having the same frequency ν_k. Such a case will not arise for non-degenerate modes of oscillation. Now if R runs through all the symmetry operations of the group G appropriate to the molecule, we get all the normal modes of oscillation belonging to the same frequency. But all these modes of oscillation may not be linearly independent.

Let $Q_1, Q_2 \ldots\ldots\ldots Q_f$ be a set of linearly independent normal co-ordinates so obtained and having the frequency ν_k. Then every other mode of oscillation with the frequency ν_k can be represented as a superposition of these f normal modes of oscillation. The oscillation is then said to be f-fold degenerate. Similarly we obtain the normal co-ordinates of different frequencies. It is now easy to see that the normal co-ordinates belonging to a definite frequency define an irreducible representation of the group G. If $Q_1, Q_2 \ldots\ldots\ldots Q_f$ are a set of normal co-ordinates with a certain frequency ν_k, the co-ordinates $Q_1, Q_2 \ldots\ldots\ldots Q_f$ combine among themselves by the application of a symmetry operation and we cannot find linear combinations of $Q_1, Q_2 \ldots\ldots\ldots Q_f$ smaller in number than f which combine among themselves by symmetry operations. Thus if

$$\bar{R}\, Q_1 = a_{11}\, Q_1 \ldots\ldots\ldots\ldots + a_{1f}\, Q_f$$
$$\bar{R}\, Q_2 = a_{21}\, Q_1 \ldots\ldots\ldots\ldots + a_{2f}\, Q_f$$
$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$
$$\bar{R}\, Q_f = a_{f1}\, Q_1 \ldots\ldots\ldots\ldots + a_{ff}\, Q_f$$

then $$R \rightarrow \bar{R} \rightarrow \text{the matrix } (a_{ij})$$

and the correspondence defines a representation. *Thus a set of normal co-ordinates of a definite frequency define an irreducible representation.*

Determination of the Number of Normal Modes that Belong to a Given Irreducible Representation.—We divide the $3n$ normal co-ordinates into different sets, each set belonging to a definite frequency. Let the irreducible representation defined by the rth set be denoted by $D^{(r)}$. Then the reducible representation of all the normal co-ordinates may be denoted by

$$R \rightarrow \bar{R} \rightarrow \triangle R = \begin{vmatrix} D^{(1)}(R) & \cdot & \cdot & \cdot \\ \cdot & D^{(2)}(R) & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{vmatrix}$$

On the other hand, the $3n$ cartesian co-ordinates $x_1, y_1, z_1 \ldots\ldots x_n, y_n, z_n$ define a reducible representation, for $\bar{R}q$ where q stands for any one of $x_1, x_2,$—z_n is a linear combination of them

and therefore defines a representation of the group. It may easily be proved that this representation is equivalent to the above representation defined by the $3n$ normal co-ordinates. Consequently the character of any group element R in the two representations is the same.

It is easy to calculate the character of any operation R for the reducible representation defined by the cartesian co-ordinates. If the symmetry operation R takes over the atom k into the atom l, we have in general $\bar{R}x_k = a_{kl}x_l + b_{kl}y_l + c_{kl}z_l$ and the character arising from x_k is 0. Similarly, the character arising from y_k and z_k is 0. If, on the other hand, the kth atom is invariant under the operation R, we have

$$\bar{R}x_k = x_k \cos\varphi + y_k \sin\varphi$$
$$\bar{R}y_k = -x_k \sin\varphi + y_k \cos\varphi$$
$$\bar{R}z_k = z_k.$$

In the above equations, the axis of rotation is taken as the Z axis itself and the X and Y axes lie in a plane perpendicular to it. There is no loss of generality in the choice of such co-ordinates as the character is independent of the choice and we obtain $1+2\cos\varphi$ for the character of an operation consisting of a rotation through φ radians. If the operation is a rotation reflection, we have the same relations as above except that z_k is replaced by $-z_k$ and the character comes out as $-1+2\cos\varphi$. A simple reflection may be taken as a rotation through 0 radians accompanied by a reflection and a centre of inversion may be taken as a rotation through π followed by a reflection. We thus arrive at the result that an invariant atom under the operation R gives rise to the character $\pm 1+2\cos\varphi_R$, the + or the − sign being used according as the operation is a pure rotation or a rotation reflection. The atoms, which are not invariant, do not contribute anything to the character of R. *Hence, in the reducible representation defined by the cartesian co-ordinates, the character of any operation R is* $U_R(\pm 1+2\cos\varphi_R)$ *where* U_R *is the number of invariant atoms under the operation R.* This will also be the character of the operation R in the representation defined by the normal co-ordinates since they are equivalent.

From a knowledge of the group characters in any representation Γ, we find n_i, the number of times a particular irreducible representation Γ_i is contained in Γ, by means of the important formula [1]

$$n_i = \frac{1}{\mathrm{N}} \sum_{\mathrm{R}} \chi_i(\mathrm{R}) \chi'(\mathrm{R}), \qquad \ldots \qquad \ldots \qquad (1)$$

where $\chi_i(\mathrm{R})$ and $\chi'(\mathrm{R})$ are respectively the characters of R in Γ_i and Γ. N is the order of the group. In our problem, Γ stands for the reducible representation of the normal co-ordinates and hence, $\chi'(\mathrm{R})$ is equal to $U_{\mathrm{R}}(\pm 1 + 2 \cos\varphi_{\mathrm{R}})$.

Application to Molecules.—The first step in the application of the foregoing theory to an actual molecule consists in ascertaining its point group G and writing down the appropriate character Table containing the characters of the various group elements for the irreducible representations of the group. The character Table in respect of each group may be obtained from the general Tables given in the text. We have then to evaluate the character of each symmetry operation in the group for the reducible representation defined by the cartesian co-ordinates in the manner already explained. Since the character is the same for all operations coming under a particular class j, we have

$$\sum_{\mathrm{R}} \chi_i(\mathrm{R}) \chi'(\mathrm{R}) = \sum_j h_j \chi_i(\mathrm{R}) \chi_j'(\mathrm{R}).$$

The summation on the right hand side extends over all the classes that constitute the group and h_j represents the number of elements in the jth class. Equation (1) of the foregoing section will now be rewritten as

$$n_i = \frac{1}{\mathrm{N}} \sum_j h_j \chi_i(\mathrm{R}) \chi_j'(\mathrm{R}). \qquad \ldots \qquad \ldots \qquad (1a)$$

A knowledge of the number of atoms that remain invariant under each of the group operations R is necessary for evaluating

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[1] The actual value of n_i is obtained when χ_i (R) is replaced by its complex conjugate but as we are dealing with real characters, this distinction is of no significance. For a proof of this and other similar relations used in this Appendix, reference has to be made to standard texts dealing with the 'Theory of Groups'.

n_i with the help of (1*a*) and this number is also easily obtained for a given molecule. n_i includes the normal co-ordinates appropriate to the pure rotations and translations of the molecule as well. If instead of $\chi_j'(\mathrm{R})$, we use a modified character $\psi_j'(\mathrm{R})$, which is the same as $\chi_j'(\mathrm{R})$ when R is a rotation reflection but equal to $(U_\mathrm{R}-2)(1+2\cos\varphi_\mathrm{R})$ when R is a pure rotation, we obtain n_i' (see 1*b*) excluding the pure rotations and translations.

$$n_i' = \frac{1}{\mathrm{N}}\sum_j h_j \chi_i(\mathrm{R})\psi_j'(\mathrm{R}) \qquad \ldots \qquad \ldots \qquad (1b)$$

Selection Rules for Fundamental Modes.[1]—We have seen that every normal mode of oscillation belongs to some one irreducible representation of the group of symmetry operations. *The mode is active or inactive in the infra-red absorption according as it causes a variation or not in the electric moment of the molecule.* This condition may be symbolically represented by

$$\sum_\mathrm{R}(\pm 1+2\cos\varphi_\mathrm{R})\chi_i(\mathrm{R})\begin{cases} = 0 \ldots \text{inactive} \\ \neq 0 \ldots \text{active.}\end{cases} \qquad \ldots \qquad (2)$$

$\pm 1+2\cos\varphi_\mathrm{R}$ is the character of the operation R in the representation defined by the vector components of the electric moment and $\chi_i(\mathrm{R})$ is the character in the irreducible representation Γ_i to which the normal co-ordinate belongs. The summation extends over all the operations that constitute the group.

The selection rule for the Raman spectra may be expressed in a like manner. *The mode is active or inactive according as it causes a variation or not in the optical polarizability of the molecule.* This condition may be symbolically represented by

$$\sum_\mathrm{R} 2\cos\varphi_\mathrm{R}(\pm 1+2\cos\varphi_\mathrm{R})\chi_i(\mathrm{R})\begin{cases} = 0 \ldots \text{inactive} \\ \neq 0 \ldots \text{active.}\end{cases} \qquad \ldots \qquad (3)$$

$2\cos\varphi_\mathrm{R}(\pm 1+2\cos\varphi_\mathrm{R})$ is the character of the operation R in the representation defined by the tensor components of the polarizability and $\chi_i(\mathrm{R})$ is the character in the irreducible representation Γ_i to which the normal co-ordinate belongs.

[1] Proofs are omitted. These may, however, be obtained from original papers.

Selection Rules for First Overtones.—The selection rules that are appropriate to the various overtones may be expressed in a similar manner. Tisza has made a very complete study of these cases and the details will not be repeated here. It may, however, be mentioned that lines of higher order are of very infrequent occurrence in Raman effect and the few cases that have been observed are limited to the first overtones. The intensity of the higher overtones is so very small that a consideration of these is not of much practical importance. We will accordingly confine our discussion to the first overtones only and quote the results of Tisza. Relation (4) gives C_i, the number of times the first overtone of a normal mode coming under a certain irreducible representation occurs in any irreducible representation Γ_i of the group.

$$C_i = \frac{1}{N}\sum_R \chi^2(R)\chi_i(R). \qquad \ldots \qquad \ldots \qquad (4)$$

In equation (4)

$$\chi^2(R) = \frac{[\chi(R)]^2 + \chi(R^2)}{2}.$$

By applying the test contained in equation (4) to all the irreducible representations of the group of symmetry operations, complete information as to the various types under which an overtone comes may easily be obtained. If all or some of these types are active, then the overtone is also active. If all the constituents are inactive, then the overtone is also inactive.

Selection Rules for Combinations.—Combinations are also of infrequent occurrence in Raman effect and we need consider only the simple case of the fundamental of one normal mode combining with the fundamental of another normal mode. The two modes that are combining may or may not belong to the same irreducible representation. Tisza has given the general theory and his result, simplified so as to be applicable to this case will be given here. Equation (5) gives C_i, the number of times a combination between two normal modes, one coming under the irreducible representation (k) and the other coming under (l), occurs in any irreducible representation Γ_i of the group.

$$C_i = \frac{1}{N}\sum_R \chi^{(kl)}(R)\chi_i(R). \qquad \ldots \qquad \ldots \quad (5)$$

In equation (5)

$$\chi^{(kl)}(R) = \chi^{(k)} \cdot \chi^{(l)}.$$

The expression is valid both when (l) is the same as (k) and different from (k). Proceeding in a manner similar to that adopted in the case of the overtones, we can express the combination as the sum of several types of motion coming under different irreducible representations. If all or some of these types are active, then the combination is also active and if all the constituents are inactive, then the combination is also inactive.

Some Special Cases.—We shall now prove a number of theorems relating to certain special cases.

1. *All modes of oscillation coming under the total symmetric class are always Raman active.* The character $\chi_i(R)$ is 1 for all R for a total symmetric class by definition. Since the combination $\alpha_{xx}+\alpha_{yy}+\alpha_{zz}$ is an invariant for all R, its character is always 1 and is therefore present in the total symmetric representation of all groups. We accordingly conclude that all modes of oscillation coming under the total symmetric class are Raman active.

2. *The first overtone of every normal mode is Raman active irrespective of whether the fundamental itself is active or not.* Since we have already proved that the total symmetric oscillation is always Raman active, in order to prove this theorem, we need only show that all first overtones occur at least once in the total symmetric irreducible representation. An inspection of (4) reveals that this is achieved if we prove that

$$\sum_R \chi^2(R) \neq 0.$$

For all non-degenerate oscillations, the character is either $+1$ or -1 for all R and $[\chi(R)]^2$ as well as $\chi(R^2)$ reduce to $+1$ for all R and the above relation is at once satisfied. In fact, the representation of such overtones is equivalent to the irreducible representation of the total symmetric type itself. In the case

of degenerate oscillations, the proof is slightly more complicated and depends on the following theorem.

$$\sum_{R}\left[\chi(R)\right]^{2} = N.$$

In order that $\sum_{R} \chi^{2}(R)$ may be zero, we should have $\sum_{R} \chi(R)^{2}$ equal to $-N$ which is never the case. Thus the overtone contains at least one component coming under the total symmetric class.

3. We may now go further and conclude that *if we are dealing with liquids or gases in which the molecules are oriented at random, the overtones may exhibit a depolarization factor less than* $\frac{6}{7}$ *irrespective of whether the Raman line due to the fundamental is polarized or depolarized.*

4. *If a centre of inversion is one of the elements in the group, all normal modes which are antisymmetric with respect to it are Raman inactive.* For every operation R, which has the character $\chi_i(R)$, there is an operation R_i obtained by combining i with R having the character $-\chi_i(R)$ in all irreducible representations which are antisymmetric with respect to i. This combination can be regarded as R followed by a rotation-reflection through π. If in the representation defined by the tensor components, the character of R is $2\cos\varphi_R(\pm 1+2\cos\varphi_R)$ then the character of R_i is $2\cos(\varphi_R+\pi)\,(\mp 1+2\cos\overline{\varphi_R+\pi})$ which is the same as $2\cos\varphi_R\,(\pm 1+2\cos\varphi_R)$. Consequently $\sum_{R} 2\cos\varphi_R$ $(\pm 1+2\cos\varphi_R)\,\chi_i(R)$ vanishes, the terms cancelling in pairs, and the mode is inactive.

5. *All normal modes which are symmetric with respect to a centre of inversion are infra-red inactive.*

This theorem may be proved in a manner analogous to the foregoing one by studying the behaviour of the character $\pm 1+2\cos\varphi_R$ in the representation defined by the vector components.

6. *If a group possessing a* p*-gonal symmetry has a plane of reflection* σ_h *as one of its elements, it follows that a centre of inversion is also an element when* p *is even and the foregoing rule applies as such.*

7. *The sum* $\alpha_{xx}+\alpha_{yy}+\alpha_{zz}$ *exists only in the total symmetric class. This has the consequence of giving a depolarization value of* $\frac{6}{7}$ *for all the Raman lines, coming under any of the irreducible representations with the exception of the total symmetric class, in the case of liquids and gases.*

Since $\alpha_{xx}+\alpha_{yy}+\alpha_{zz}$ is an invariant for all R, its character is always 1 and therefore it comes only under the total symmetric class. By virtue of the orthogonality relations, it does not come in any other representation.

8. *All Raman active normal modes combine with each one of the modes coming under the total symmetric class to give Raman active combination tones. On the other hand, the combination of an inactive mode with a mode belonging to the total symmetric class is also inactive.* This follows from the fact that the characters of the combination of any mode with one coming under the total symmetric class remain the same as those of the original itself.

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